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SERIES A, VOL. 206, pp. 1–67.

THE COMBINATION OF HYDROGEN AND OXYGEN IN CONTACT WITH HOT SURFACES

BY

WILLIAM ARTHUR BONE, PH.D., D.SC., F.R.S.,
LATE BISHOP BERKELEY FELLOW OF OWENS COLLEGE, MANCHESTER, AND FELLOW OF VICTORIA UNIVERSITY,

AND

RICHARD VERNON WHEELER, B.SC.,
DALTON SCHOLAR AND FELLOW OF MANCHESTER UNIVERSITY.

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I. *The Combination of Hydrogen and Oxygen in Contact with Hot Surfaces.*

By William Arthur Bone, *Ph.D., D.Sc., F.R.S., late Bishop Berkeley Fellow of Owens College, Manchester, and Fellow of Victoria University, and* Richard Vernon Wheeler, *B.Sc., Dalton Scholar and Fellow of Manchester University.*

Received November 14,—Read December 7, 1905.

A large number of observations on the rates of chemical reactions in homogeneous systems, *e.g.*, in solutions, has proved that the velocity of a given reaction is determined by its order in accordance with the principle of mass action. It has been frequently assumed that the velocities of gaseous reactions are governed by the same law, although the few measurements which have been so far made hardly justify the assumption. Take, for example, the decomposition of arsine, the velocity of which was determined by enclosing the gas, at atmospheric pressure, in a glass bulb maintained at 310° and recording the pressure at the end of successive time intervals.[*] The results showed that the velocity of decomposition is directly proportional to the concentration of the arsine. On the assumption that the rate of change was governed by the law of mass action, it was concluded that the decomposition was a monomolecular one. But it is known that at temperatures below about 1000° the vapour of arsenic consists of tetratomic molecules, and, therefore, the equation for the decomposition of arsine at 310° must be written

$$4AsH_3 = As_4 + 6H_2.$$

If so, then assuming that the decomposition takes place in a homogeneous system, its velocity should, according to theory, be proportional to the fourth power of the arsine concentration, and not to the first power as the experiment proves it to be. The discrepancy here indicated has been explained by the further assumption that the reaction really proceeds in stages, as follows:—

(*a*) The monomolecular decomposition of arsine at finite velocity

$$AsH_3 = As + 3H;$$

---

[*] D. M. Kooij, 'Zeit. Phys. Chem.,' 1892, vol. 12, p. 155; J. H. Van 't Hoff, 'Studies in Chemical Dynamics' (1896), p. 2.

(*b*) The subsequent combinations of (1) four arsenic atoms forming the complex As_4, and (2) two hydrogen atoms forming H_2, both combinations taking place with relatively infinite velocities.

The recent determinations of the velocity of the decomposition of ammonia in porcelain vessels at high temperatures by Dr. PERMAN and Mr. ATKINSON[*] indicate that it is always proportional to the first power of the ammonia concentration. The authors concluded that the decomposition "is monomolecular, proceeding according to the equation $NH_3 = N + 3H$; the union of the atoms to form molecules is probably so quick that it can be neglected when compared with the rate of decomposition of the ammonia molecule" (p. 116).

It may, however, be seriously questioned whether the above assumptions are admissible: whether, in such cases, we are dealing with a chemical change in a homogeneous system to which the principle of mass action can be applied.

In discussing the velocities of gaseous reactions, the catalytic influence of the heated surface to which the gases are exposed, *i.e.*, the walls of the containing vessel, or any solid material with which it may be packed for the purpose of accelerating the reaction, has hitherto not received the attention it deserves. Many workers have investigated the combination of gases in glass vessels at elevated temperatures, and it is generally agreed that, in a large number of cases, the chemical change is mainly, if not entirely, confined to the layer of gas immediately in contact with the surface. We may here recall the many independent attempts of VAN 'T HOFF and VICTOR MEYER to measure the velocity of the interaction of hydrogen and oxygen in glass bulbs, at temperatures below the ignition point. Their efforts were, however, frustrated by the controlling influence of the "surface factor." It would appear, therefore, that whatever may be the mechanism of the "surface action," the gas actually lying on the surface is in a different condition from the main body of the gas, and that this condition is more favourable to chemical interchanges. The system is, therefore, not homogeneous, and the law of mass action does not generally apply to it.

The power possessed by platinum and certain other metals of inducing the combination of hydrogen and oxygen at low temperatures engaged the attention of many eminent investigators during the early part of last century. In 1817 Sir H. DAVY[†] discovered that a warm spiral of platinum wire will bring about the ignition of hydrogen, and in the next year ERMAN[‡] found that electrolytic gas may be fired by such a spiral warmed to 50° only. The subject was, however, first systematically investigated by DULONG and THÉNARD[§] and, independently, by DÖBEREINER[||] in the year 1823. DULONG and THÉNARD found that the activity of platinum is enhanced by immersion in hot nitric acid, followed by a rapid washing with distilled water. The activity thus imparted is lost on exposure to the atmosphere, more quickly in damp than in dry weather, but may be restored either by ignition followed by rapid cooling, or by treatment with nitric acid. Finely divided silver was found to induce the combination of the gases at 150°, thin gold leaves at 260°, whilst fragments of non-metallic substances, such as charcoal, pumice-stone, porcelain, rock crystal and glass exhibited the power at temperatures below 350°. In the case of glass, it was observed that angular pieces were approximately twice as effective as spherical masses of equal surface. DÖBEREINER discovered that freshly prepared platinum black absorbs oxygen from the air, and when thus charged will cause the formation of steam when plunged into a jar of hydrogen. The operation of alternately charging the metal and then burning away the oxygen in hydrogen can, he found, be repeated many times. The platinum thus appeared to act as a carrier of oxygen to the hydrogen.[*]

---

[*] 'Roy. Soc. Proc.,' 1904, vol. 74, p. 110.

[†] 'Phil. Trans.,' vol. 107, 1817, p. 77; 'Quart. Journ. of Science,' vol. V., 1818, p. 128.

[‡] 'Abhandlungen der Akadèmie der Wissenschaften in Berlin für 1818–1819,' p. 368.

[§] 'Ann. Chim. Phys.,' vol. 23, 440; vol. 24, 380.

[||] 'Schw.,' 34, 91; 38, 321; 39, 159; 42, 60; 63, 465.

This conclusion was, however, criticised by FUSINIERI[†] in 1825, who, on physical grounds, advocated the view that the function of the platinum is to condense the hydrogen on its surface. This view derived some support from the observation of WILLIAM HENRY[‡] that when a platinum ball is immersed in a mixture of equal volumes of electrolytic gas and ethylene, the hydrogen and oxygen alone combine, no combination of the hydrocarbon occuring unless the original mixture contained a much larger proportion of electrolytic gas. This important result was confirmed by GRAHAM in 1829.[§]

In 1834 FARADAY[||] found that if platinum electrodes are employed in the electrolysis of dilute sulphuric acid, the anode acquires the power of inducing the combination of electrolytic gas to a very high degree, whereas the cathode only becomes feebly active. He attributed the activity of the metal to its power of condensing the hydrogen and oxygen on its surface; the "condensed" gases then combine at the ordinary temperature. This theory was strongly opposed by DE LA RIVE,[¶] who revived the idea that the metal acts simply as a carrier of oxygen to the combustible gas, the catalytic process being essentially a series of alternate oxidations and reductions. In support of the "oxygen" theory, he urged the fact that when an alternating current is sent through acidulated water between platinum electrodes, the latter become covered with a fine black powder, produced by the repeated oxidation and reduction of the metal. He further showed that platinum foil rendered active by any of FARADAY's methods will absorb oxygen but not hydrogen.

---

[*] 'LIEBIG'S Annalen,' XIV. (1835), p. 10.

[†] 'Giorn. di Fisica,' VII. (1824), pp. 133, 371, 443; VIII. (1825), 259; IX. (1826), p. 46.

[‡] 'Annals of Philosophy,' 1825, vol. 25, p. 416.

[§] 'N. Quart. Journ. of Science,' vol. 6, p. 354.

[||] 'Experimental Researches in Electricity,' I., p. 165; 'Phil. Trans.,' 1834, Part I., p. 55.

[¶] 'Pogg. Annalen,' 46, 489; 54, 386.

We may now consider, *à priori*, the factors which may determine the velocity of an irreversible gaseous reaction of the type A + B = AB in a heterogeneous system. Regarding the matter from the kinetic standpoint, the observed rate of change will, in the absence of other disturbing factors, depend on (1) the actual rate of combination at the surface; (2) the rates at which A and B, respectively, diffuse inwards from the inert atmosphere outside on to the surface; and (3) the rate at which the product AB diffuses outwards. NERNST[*] has recently advanced a general theory of reactions in heterogeneous systems based on measurements of the rates of solution of salts in water, or of metals and such substances as magnesia, marble and metallic hydroxides in acids. He assumes that, for all practical purposes, the rate at which equilibrium is established at the limiting surface between the two phases (solid-liquid or solid-gas) is infinitely great compared with the rates of diffusion of the reacting substances on to, or of the reaction product away from, the surface. Hence the velocity observed in the system will depend not on the "order" of the reaction, but on the diffusion factors only. Our experiments have proved that this "diffusion" theory is incapable of explaining the facts of the catalytic combination of hydrogen and oxygen. There are clearly other factors which have a determining influence on the course of events.

BODENSTEIN'S *Experiments.*

In the year 1899 M. BODENSTEIN[†] published the results of experiments on the non-explosive combination of electrolytic gas during its passage through a glazed porcelain tube heated in a lead bath to various temperatures between 482° and 689°. The author was himself conscious of certain inherent sources of error in his experimental method, which influenced the results quite irregularly and often in a very annoying manner ("in oft recht unliebsamer Weise"). In view of this admission it is difficult to say what is the precise significance of his work. Whilst fully recognising that he was dealing with a surface phenomenon entirely, BODENSTEIN concluded that it is impossible to deduce any mathematical expression for his results other than the equation for a reaction of the third order. This, of course, means that, notwithstanding the fact that the reaction was entirely confined to the layer of gas immediately in contact with the walls of the reaction vessel, its velocity was governed by its "order" in accordance with the law of mass action. We shall, however, have no difficulty in proving that this conclusion is wrong.

---

[*] 'Zeit. Phys. Chem.,' 1904, vol. 47, p. 52. In applying the theory to the special case of catalytic gas reactions, NERNST remarks, "Da diese Reaktionen wohl ausschliesslich an der Grenzfläche des Katalysators abspielen, so wird die Geschwindigkeit keineswegs durch den Mechanismus der betreffenden Reaktion, sondern wenn, was allerdings von vornherein nicht sicher ist, der Katalysator während des Reaktionsverlaufes konstante Beschaffenheit behält und zugleich mit praktisch unendlicher Geschwindigkeit die betreffenden Substanzen an der Grenzfläche zur Reaktion bringt, auch hier lediglich durch die Diffusion der reagierenden Stoffe zum Katalysator bedingt werden," p. 55.

[†] 'Zeit. Phys. Chem.,' 1899, vol. 29, p. 665.

In 1903 **Bodenstein**[*] published a second paper dealing with the combination of hydrogen and oxygen in contact with a catalysing surface of platinum at the ordinary temperature. The experiments described are divided into two series. In the first series, the platinum surface was kept at the same temperature as the surrounding gas, so that a film of water formed on the surface. Under these conditions, the velocity of the reaction was found to be approximately proportional to the pressure of the electrolytic gas present, any excess of either hydrogen or oxygen merely acting as a diluent. This was explained on the "diffusion" theory by assuming an infinitely great rate of combination at the surface, and that therefore the observed rate depends on the rate of solution of oxygen, or on that of hydrogen when the gas contains an excess of oxygen, in the water film. But whilst the results of the published experiments support this theory, the author admits that others (unpublished) did not.[†]

In the second series of experiments, the surface of the metal was kept dry by maintaining it at a slightly higher temperature than the surrounding gas. Here the absolute rate of combination was much greater than in the first series of experiments, and it no longer, even approximately, conformed to an equation of the first order. In one experiment, for instance, where "normal" electrolytic gas was employed, the "velocity constant," $\left(k = \frac{1}{t} \log \frac{C_0}{Ct}\right)$, increased from 0·038 to 0·117, or by more than 200 per cent., as the pressure in the apparatus fell from 750 to 24·5 millims. in 14 minutes. In other experiments the values of "k" similarly increased by 100 per cent.

In connection with their researches on the mechanism of hydrocarbon combustion, the authors devised a circulation apparatus which is well adapted for measuring the velocities of catalytic gas reactions, where the product can be quickly removed from the sphere of action either by condensation, or by solution in water or other absorbing liquid. It was therefore decided to make a systematic study of the case of hydrogen and oxygen, in the hope of obtaining sufficiently reliable data to discriminate between the various possible explanations of the action of surface in inducing gaseous reactions. And, in order to avoid the danger of errors arising from a too restricted view of the phenomena, it was decided to examine in detail the action of a great variety of surfaces, including porous porcelain, magnesia, platinum, gold, silver, nickel, copper, and certain easily reducible metallic oxides, such as copper oxide, nickel oxide, and a mixture of ferric and manganous oxides obtained by calcining spathic iron ore. Bartya was also examined, but with less satisfactory results, owing to constant variations in its catalysing power, which seriously affected the velocity measurements.

In the case of an oxidisable metal, or a reducible oxide, it seems necessary to distinguish in principle between the purely "catalytic" combination of the gases without any permanent oxidation or reduction of the surface and ordinary chemical processes which do involve such permanent changes. The experiments with reducible oxides, and more particularly those with copper oxide, show that the two kinds of change are quite distinct in character. It is usually not difficult in such cases to find a range of temperature within which the purely catalytic process goes on uncomplicated by the other kind of change, and it is with the mechanism of the former that we are alone concerned in this paper.

---

[*] 'Zeit. Phys. Chem.,' 1903, vol. 46, p. 725.

[†] In this connection he remarks, "bei allen späteren (Versuchen) war der Anschluss an die zu Grunde gelegte Gleichung ein merklich schlechterer, und eine ganze Anzahl Beobachtungen wurden gemacht, die zu der Annahme der unendlich grossen Verbrennungsgeschwindigkeit nicht stimmen . . . ." (p. 737).

Although the research has revealed important minor differences between the action of the various surfaces examined, the results, as a whole, leave no room for doubt but that the catalytic process depends primarily on a condensation of one or other (and, in some cases, possibly both) of the reacting gases on the heated surface. Any purely chemical explanation of the phenomena, such, for instance, as the theory of a rapidly alternating series of oxidations and reductions of the catalysing material, seems quite inadmissible. Equally certain is it that the rate at which the gases combine over a given surface is governed neither by the "order" of the reaction, nor by diffusion factors simply.

The catalysing power of a new surface usually increases up to a steady maximum when successive charges of electrolytic gas are circulated over it. After the attainment of this steady state, the rate of steam formation is always directly proportional to the pressure, provided that the gases are present in their combining ratios, and that the product is rapidly removed from the sphere of action. In other words, the velocity curve for electrolytic gas is always of a "monomolecular" type, after the surface has acquired its "normal" degree of activity. This applies to all the surfaces examined.

When one or other of the reacting gases is present in excess, the rate of combination is nearly proportional to the partial pressure of the hydrogen, which thus becomes the determining factor in any given experiment. The case of copper oxide, and to a certain extent that also of silver, proved to be exceptional in this respect; these cases will be fully discussed later. The whole evidence of the research shows that, except in the case of copper oxide, the hydrogen plays an all important rôle in the catalytic process, being rendered "active" by association with the surface. In the majority of cases the hydrogen is merely "occluded," but in the case of silver there is evidence of chemical combination, that is to say, of the formation of an unstable hydride at the surface. In conformity with this view, the catalysing power of many of the surfaces examined (*e.g.*, porcelain, magnesia, silver, gold, platinum, and nickel) could be stimulated, often in a very high degree, by previous exposure to hydrogen at moderately high temperatures.

In this connection reference must be made to the recent researches of MM. PAUL SABATIER and JEAN SENDERENS,* which have drawn attention to the remarkable power of many metallic surfaces (and especially nickel) of rendering hydrogen "active" at comparatively low temperatures. In illustration of their results we need only give the following typical instances of direct "*hydrogenations*" effected by passing a mixture of the substance in question with hydrogen over finely divided and freshly reduced nickel. In this way hydrocarbons of the olefine series were quantitatively converted into the corresponding paraffins at 160°, and benzene yielded cyclo-hexane. Nitrobenzene was directly reduced to aniline, whilst nitromethane was converted into methylamine at 150° to 180°, and into methane and ammonia at 350°. The most remarkable results of all, however, were obtained with a mixture of carbon monoxide (1 volume) and hydrogen (3 volumes), which the authors state was completely transformed into methane and steam when passed over finely divided nickel at 250°.

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* 'Comptes Rendus,' (1899), 128, 1173; (1900), 130, 1559, 1761; (1901), 132, 210, 1254; (1901), 133, 321; (1902), 134, 514, 689, 1127; (1902), 135, 87, 225; (1903), 137, 301.

Whilst there can be no gainsaying the facts relative to the extraordinary "activity" of hydrogen when it is condensed or occluded by many surfaces, metallic and otherwise, opinions will probably differ as to the cause of the "activity." Many will attribute it to the dissociation of the hydrogen molecule at the moment of occlusion, whilst others will possibly connect it with some influence of hydrogen upon the rate of emission of ions by the surfaces involved. The experiments of Dr. H. A. WILSON on "The Discharge of Electricity from Hot Platinum"[*] are very suggestive in this connection. He found that hydrogen has an enormous influence on the negative leakage from a clean platinum wire at high temperatures. Thus at 1350°, for a given potential difference, the leakage in hydrogen, at 0·014 millim. pressure, was 25,000 times greater than the corresponding leakage in air. The leakage was, moreover, proportional to the pressure and depended on the hydrogen actually occluded by the metal. These experiments were made at much higher temperatures than any employed in our research, but Professor J. J. THOMSON has recently found that the rate of emission of negative corpuscles by alkali metals at the ordinary temperatures is greatly increased whilst they are absorbing hydrogen.[†] It should also be mentioned that the Reverend P. J. KIRKBY, who has qualitatively examined the effects of electrically heating a platinum wire (to *circa* 275°) in electrolytic gas at low pressures (40 millims. and under), concludes that the catalytic combination is "probably connected with the corpuscular discharge which is known to be emitted by platinum."[‡] It therefore seems possible that the results obtained by the above investigators and those recorded in this paper may have a common explanation. Whether or not the emission of negative corpuscles by a metal under the influence of hydrogen would induce the combination of the gases immediately in contact with the surface is a question for further investigation.

Our experiments with reducible oxides, and particularly those with copper oxide, are of special interest in that they prove how inadequate is any purely chemical view of the catalytic process. In the case of ferric and nickel oxides it is possible, within certain temperature limits, to obtain a truly catalytic combination at a rate far in excess of that at which either the surface itself is reduced by hydrogen alone, or the reduced surface reoxidised by oxygen. In the case of copper oxide, it would appear that the catalytic process primarily involves the condensation of "active" oxygen at the surface, and that the film of condensed oxygen actually protects the surface from the attacks of hydrogen; indeed, the substitution of inert nitrogen for the oxygen of electrolytic gas always produces a very remarkable acceleration of the rate at which the hydrogen disappears.

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[*] 'Phil. Trans.,' A, vol. 202, (1903), p. 243.

[†] 'Phil. Mag.,' 6th series, vol. X. (1905), p. 584.

[‡] 'Phil. Mag.,' 6th series, vol. X, (1905), p. 467.

One of the chief difficulties encountered in experiments of the kind under discussion is the reattainment of the state of "normal" activity in a given series of experiments, possibly extending over many days or even weeks together, during the course of which conditions other than temperature are purposely varied. Indeed, the certainty with which the surface can be restored to its "normal" state after a given change of conditions is often a criterion of the value of the series. It is always important, in interpreting the results of a particular set of experiments, to take into account the past history of the surface, and to follow carefully any changes in its catalytic power induced by special circumstances. Throughout the paper, therefore, the experiments with a given surface are described in their chronological order, and the date on which each experiment was performed is indicated in the tabulated results.

An Apparatus for Measuring the Velocities of Catalytic Gas Reactions.

The apparatus employed for measuring the velocity of the catalytic combination of hydrogen and oxygen during this research is shown in Diagram I., fig. 1. It is, however, well adapted for velocity measurements in the case of other catalytic gas reactions when the product can be removed by condensation or absorption by a suitable reagent.

It consists essentially of a closed system in which the reacting gases are circulated, at a uniform rate, over the particular surface under investigation, maintained at a constant temperature, and afterwards through a cooling or absorption arrangement to ensure the rapid removal of the reaction product, in this case steam. The rate of combination is, in the case under discussion, measured by observing the pressure in the apparatus at regular intervals of time. By means of a series of "bye-pass" sampling tubes, samples of the gases can, if necessary, be cut off at intervals during an experiment without altering the pressure in the apparatus, or in any way interfering with either the course or the conditions of the reaction.

Two great advantages may be claimed for this apparatus, namely, (1) that with ordinary electrolytic gas it allows of velocity measurements being made in a single

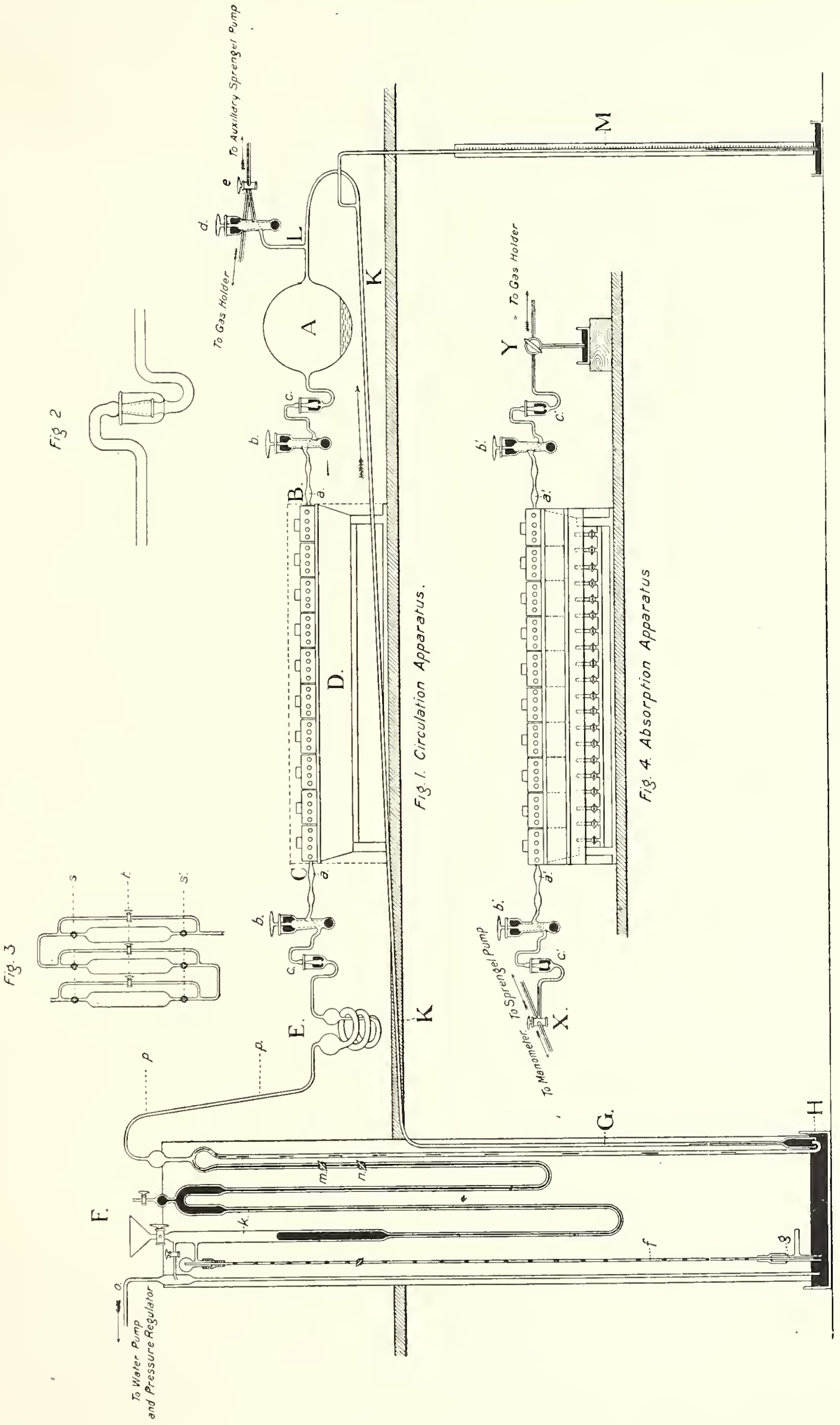

Fig. 1. Circulation Apparatus.

Fig. 4. Absorption Apparatus

Diagram I.

experiment over a wide range of pressure (from about 500 millims. to as low as 20 millims.), so that practically the whole velocity curve may be determined, and (2) that in cases where the gases are not originally present in their combining ratio, it is possible to follow the variations of the velocity with an ever increasing excess of one of them.

The glass globe A (capacity = about 1200 cub. centims.) serves merely as a reservoir for the reacting gases; it contains a few cubic centimetres of distilled water, so that the gases are kept saturated with aqueous vapour at the room temperature (which is indicated by a thermometer placed with its bulb in contact with the outer wall of the globe).

From the globe the gases are drawn by the automatic Sprengel pump F (the "circulating pump"), at a uniform rate, through the Jena hard glass combustion tube BC, containing the surface under examination, and which is heated in the Lothar Meyer constant temperature furnace D. This furnace is protected from draughts by a thick asbestos hood (indicated by dotted lines in the diagram), at each end of which are arranged suitable screens in order to shield the rest of the apparatus from radiated heat. The gas supply of the furnace is regulated by a Stott's governor, which keeps the temperature constant for, if necessary, many days together.

Each end of the combustion tube is fitted with special glass joints (*aa*) composed of rings of glass of gradually diminishing hardness fused together, ending ultimately in a grade of glass soft enough to allow of its being fused direct on to the mercury cup taps *bb*. The adoption of these special joints obviated the use of any indiarubber connections in the apparatus. The mercury cup taps, *bb*, are in turn connected, by fused glass joints, with the ground glass joints *cc*, each of which works under a mercury seal. An enlarged drawing of one of these joints is shown in the diagram (fig. 2). This device allows of the ready removal of the entire combustion tube, and its transference to similar mercury sealed joints, *c'c'*, in the "absorption apparatus" (fig. 4), to be described later.

On leaving the combustion tube the gases pass through a glass worm, E, surrounded by a water jacket (not shown in the diagram), through which a stream of cold water is constantly maintained, to ensure the rapid cooling of the hot gases and the condensation of steam. The cooled gases then pass onwards to the automatic Sprengel pump F, which delivers them up into the vertical tube, G, standing over mercury in the trough H; thence they pass along the horizontal tube, KK, back again into the globe A, thus completing the circuit.

The apparatus is closed by the mercury cup tap, *d*, sealed into the ⊥-piece L. The other side of *d* is connected, by a fused glass joint, with the three-way tap *e*, through which communication may be made either with the gas-holder containing the experimental mixture, or with an auxiliary automatic Sprengel pump used for the rapid exhaustion of the apparatus as circumstances require. The pressure in the apparatus at any given moment is indicated by the mercurial gauge M, fused into the horizontal tube KK at a point near to the globe A.

It is necessary for the complete success of a given series of experiments that the rate of circulation shall be maintained strictly uniform for, if need be, many days together. This was secured by automatically regulating the suction of the water pump employed to work the Sprengel circulating pump.

The suction of the water pump, applied at *o*, raises mercury from the trough H, a short distance up the tube *f*, which just rests on the surface of the mercury. The mercury is broken up into short threads by the entrance of air (filtered through cotton-wool) through the horizontal arm of the wider T-piece *g*, the vertical branch of which reaches to the bottom of the trough H. The force is now sufficient to drive the short threads up to the top of the tube *f*, whence they fall into the reservoir *k*. The circulation of the gases in the apparatus can be adjusted to any desired rate, within considerable limits, by means of the stop-cocks *m*, *n*, which serve to regulate the flow of mercury down the full tube of the circulating pump.*

The capacity of the whole apparatus is about 1500 cub. centims., that of the combustion tube only about 75 to 125 cub. centims., according to the closeness with which it is packed with the catalysing material. In considering the experimental results, it is useful to remember that the dimensions of the apparatus are such that a fall in pressure of, say, x millimetres during a given time interval corresponds to the combination of as nearly as possible $2x$ cubic centimetres of the reacting gases $(2H_2+O_2)$.†

Sampling of the Gases during an Experiment.

It was frequently desirable, and sometimes necessary, to check the pressure records by analysing samples of the gas cut off at regular intervals during an experiment. In order to do this without altering the pressure in the apparatus, or interfering with the course of the reaction, the device of "bye-pass" sampling tubes shown in Diagram I., fig. 3, was employed. When required, these tubes were fused into the circulation apparatus, between the worm E and the circulating pump F, at points indicated by the dotted lines *pp*. At the beginning of an experiment the taps *ss* at the ends of each of the tubes were opened, and the taps *tt* in the "bye-passes" closed. It was thus only necessary to close the taps *ss* at each end of one of the tubes and to open the tap t in the corresponding "bye-pass" to shut up a sample of the gas at any given moment. At the conclusion of the experiment, after the rest of the apparatus had been exhausted, the contents of each sampling tube could be successively withdrawn through the pump for analysis.*

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* The rate of circulation, which is, of course, strictly uniform throughout a given series of experiments, can be varied in different series, so that the gases can be made to complete a circuit in from 30 to about 120 minutes. Such abbreviated expressions as "rate of circulation = 1 in 30 minutes," often used throughout this paper, mean a rate such that the gases completed the circuit once every 30 minutes.

† For the purposes of this research two circulation apparatuses were installed in the laboratory. This not only effected a considerable economy of time, but it also permitted of simultaneous examinations of the action of two different surfaces. This plan was so advantageous that during part of the research a third apparatus was requisitioned.

Preparation of the Gases.

The electrolytic gas employed during the research was prepared by the method recommended by Mr. H. BRERETON BAKER,† namely, by the electrolysis of a solution of highly purified barium hydroxide. This method ensures its freedom from hydrocarbon impurity, ozone, or hydrogen peroxide, [and repeated careful analyses showed that its constituents were present in exactly their combining ratio.—*February* 10, 1906.]. The gas was collected in a graduated glass holder, fitted with ground-glass joints, over a mixture of equal volumes of pure glycerine and water. From this holder the gas was passed direct into the circulation apparatus, as required. When it was necessary to experiment with mixtures originally containing an excess of one of the reacting gases, the electrolytic gas was mixed in the holder with a known proportion either of hydrogen, prepared electrolytically from a solution of barium hydroxide, or of oxygen, prepared by heating recrystallised potassium permanganate.‡

Experimental Method.

Throughout a given series of experiments the gas supply of the furnace was never interfered with, so that the combustion tube was kept at the desired constant temperature day and night, not only during each experiment, but also during the intervals between two experiments. In this way perfect uniformity of temperature conditions was secured. At the outset of an experiment, the circulation apparatus was thoroughly exhausted by bringing the auxiliary Sprengel pump into action. The experimental mixture was then admitted to the vacuous apparatus, and five minutes later the first pressure reading was taken. Subsequent pressure readings were taken at regular intervals up to the end of the experiment; these readings, corrected for small variations in the room temperature and for the pressure of water vapour, gave a direct measure of the reaction velocity. The time intervals were determined by a chronograph recording stop-watch.

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* [It should be stated that all the gas-analyses in connection with the research were carried out over mercury in an improved form of McLeod apparatus described by one of the authors in the 'Proceedings of the Chemical Society,' vol. XIV. (1898), p. 154.—*February* 10, 1906.]

† 'Journal of the Chemical Society,' vol. LXXXI. (1902), p. 400.

‡ The expression "normal electrolytic gas," used throughout this paper, means electrolytic gas *without* any addition of oxygen or hydrogen.

The Absorption Apparatus.

Whenever it was necessary to test the power of a given surface to absorb hydrogen (or oxygen) at higher temperatures than could be obtained with the Lothar Meyer furnace of the circulation apparatus, the combustion tube containing the catalysing material was transferred to the "absorption apparatus" shown in Diagram I., fig. 4. This consisted of a high-temperature furnace, properly screened by an asbestos hood and placed symmetrically with regard to the two ground-glass mercury cup joints *c′c′*, into which the combustion tube exactly fitted. One of these joints was fused on to the three-way tap X, through which connection could be made either with an automatic Sprengel pump or a syphon manometer. The other joint was similarly fused to the tap Y, which served to connect the apparatus with the gas-holder containing the hydrogen (or oxygen). In making an experiment, the combustion tube was first of all thoroughly exhausted and heated to the desired experimental temperature (usually about 650°), which was kept constant by the employment of a Stott's governor in connection with the gas supply of the furnace. The gas under examination was then admitted from the holder, and the absorption (if any) followed by taking pressure readings every few minutes. When the material was fully charged, the furnace was turned out and the unabsorbed gas pumped out in the cold. Finally, the combustion tube was again heated to the experimental temperature and any occluded gas pumped out and collected for examination. In this way the rapidity and extent to which a given surface occluded the gas was measured, and, by afterwards transferring the combustion tube with its contents back again to the circulating apparatus, the influence of repeated occlusions on its catalysing power was determined.

PART I.—EXPERIMENTS WITH POROUS PORCELAIN.

In these experiments the combustion tube of the apparatus was closely packed with fragments of unglazed porous porcelain which had been previously heated to 1000° in a muffle furnace. The material was perfectly white in colour and presented a large surface to the reacting gases. Its average composition was as follows:—

	Per cent.		Per cent.
Silica	75·75	Calcium oxide	1·45
Alumina	21·30	Magnesium oxide	0·35
Ferric oxide	0·05	Sodium and potassium oxides .	0·70

During the course of the research, altogether five different surfaces of this material were employed. The results obtained with all five surfaces were the same in three important particulars, namely (1) that with normal electrolytic gas the rate of combination was always proportional to the pressure of the dry gas; (2) that with an excess of either of the two reacting gases the rate of combination was always mainly, if not entirely, proportional to the partial pressure of the hydrogen; and (3) that the catalysing material occluded hydrogen, but not oxygen, at dull red heat.

First Series.—Normal Electrolytic Gas with Surface A *at* 450°.

The following two experiments were made at the outset of the research with the object of testing Bodenstein's statement that the rate of combination in contact with porcelain is in accordance with the equation for a reaction of the third order (*loc. cit.*). The material was less porous than that used in most of the subsequent experiments, and the rate of circulation considerably slower, namely, a complete circuit in about two hours. The temperature of the combustion tube was 450° throughout each experiment, and pressure records were taken every twelve hours. In the following tables:—

t = time in hours from the beginning of each experiment;
T = temperature of the combustion tube;
P = corrected pressure of the dry gas in the apparatus;
k_1, k_2 and k_3 are the "constants" calculated from the equations for reactions of the first, second and third orders respectively.

Experiment I.					Experiment II.				
October 29 to November 2, 1903. T = 450°. Rate of circulation = 1 in 120 minutes.					November 4 to 9, 1903. T = 450°. Rate of circulation = 1 in 120 minutes.				
t.	P.	k_1.	$k_2 \times 10^6$.	$k_3 \times 10^8$.	t.	P.	k_1.	$k_2 \times 10^6$.	$k_3 \times 10^8$.
hours.	millims.				hours.	millims.			
0	469·4	—	—	—	0	465·6	—	—	—
12	330·4	0·0127	75	19	12	324·0	0·0131	78·2	20
24	229·0	0·0129	93	30	24	228·6	0·0129	92·8	30
36	167·2	0·0124	107	43	36	163·9	0·0126	109·8	45
48	120·9	0·0123	128	67	48	116·1	0·0125	134·7	72
60	89·4	0·0120	151	100	60	84·6	0·0123	161·2	112
72	66·2	0·0118	180	155	72	60·7	0·0123	199·0	185
84	48·3	0·0117	221	252	84	42·9	0·0123	251·9	321
96	36·0	0·0116	267	400	96	28·6	0·0126	341·8	634
108	27·8	0·0113	313	597	108	20·6	0·0125	429·5	1088
120	21·0	0·0112	379	943	120	14·6	0·0125	552·7	1931

The pressure curve for Experiment II., which is reproduced in Diagram II., Curve A, shows how regular was the rate of combination throughout the five days over which the observations extended.

These results prove conclusively that with normal electrolytic gas the rate of

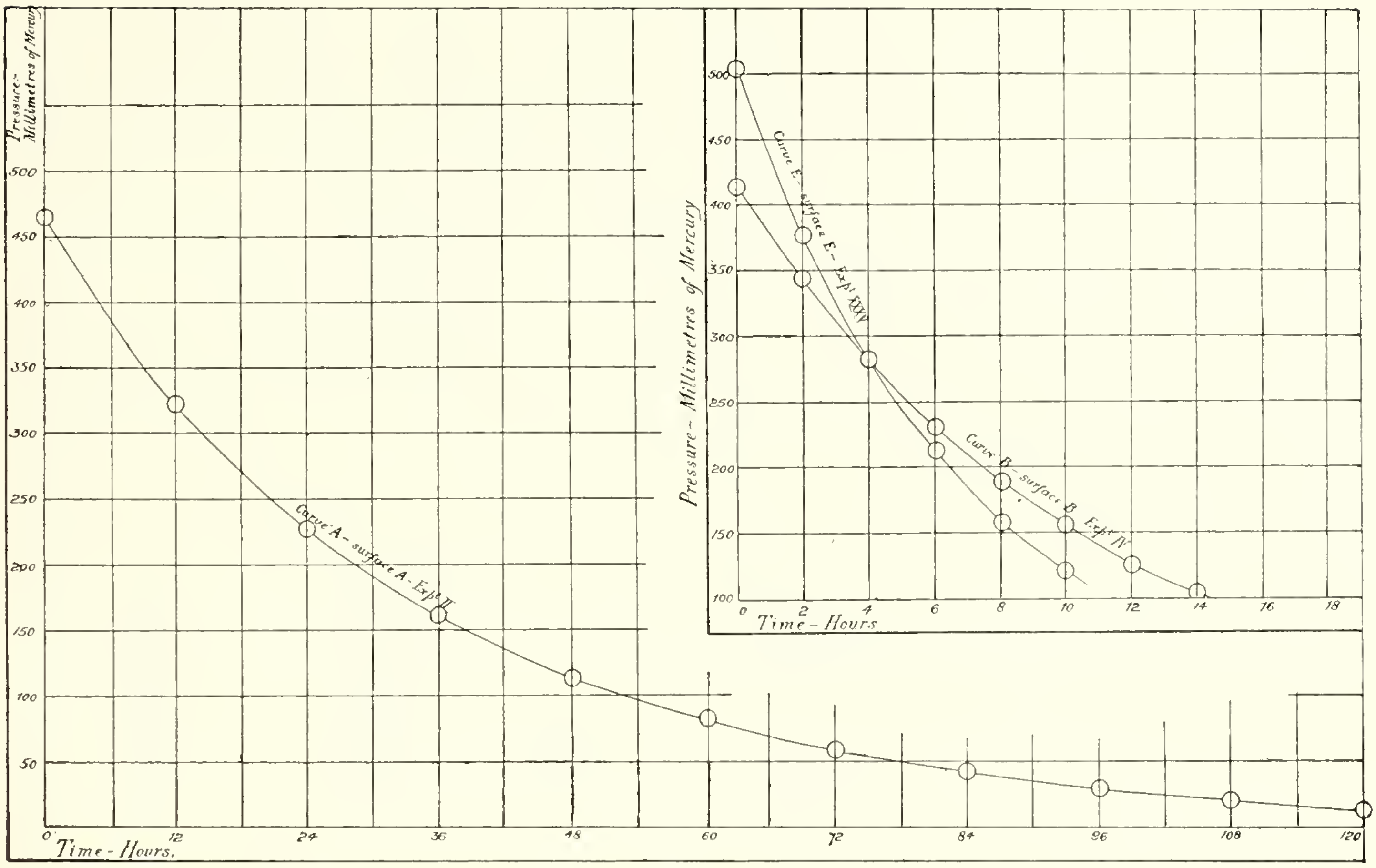

Diagram II. Experiments with porcelain. Pressure curves for normal electrolytic gas.

combination is proportional to the pressure of the dry gas, the values of "k_1," calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$, being remarkably constant throughout each experiment, even though the total pressure varied over a wide range.

Second Series.—Experiments with Surface B at 430°.

This surface had been previously used for experiments on the catalytic combination of carbon monoxide and oxygen, during the course of which it had settled down to a very steady condition as regards its catalysing power. Before being packed into the combustion tube of the apparatus, the material was thoroughly burnt out at red heat in a current of air. Neither the tube nor its packing was changed throughout the whole of the following series of experiments (III. to XX. inclusive), which may be sub-divided into three groups, according to the special objects in view in each case.

1*st Group.—With Normal Electrolytic Gas.*

This group comprised two experiments with normal electrolytic gas. In Experiment III. the rate of circulation was 1 in 20 minutes, and in IV. 1 in 30 minutes, otherwise the conditions were the same. As might be expected, the absolute rate of combination was greater in III. than in IV. The values of "k_1" given in the following table are calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$; it will be seen that in each experiment the rate of combination varied directly with the pressure of the dry gas.*

EXPERIMENT III. March 7, 1904. T = 430°. Rate of circulation = 1 in 20 minutes.			EXPERIMENT IV. March 14, 1904. T = 430°. Rate of circulation = 1 in 30 minutes.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	406·7	—	0	411·8	—
2	322·5	0·0503	2	343·3	0·0395
4	259·4	0·0486	4	283·5	0·0405
6	203·0	0·0501	6	230·3	0·0420
8	159·6	0·0507	8	188·5	0·0424
10	125·5	0·0510	10	155·6	0·0422
12	97·1	0·0519	12	126·2	0·0424
14	76·1	0·0520	14	106·0	0·0422
16	58·7	0·0526			

The pressure curve for Experiment IV. is shown in Diagram II., Curve B, p. 15. The gas remaining in the apparatus at the end of Experiment IV. was withdrawn and analysed; it contained

$$H_2 = 66·1, \quad O_2 = 33·2, \quad \text{and} \quad N_2 = 0·7 \text{ per cent.}†$$

The nitrogen would correspond to rather less than 0·2 per cent. in the original gas.

2nd Group.—Showing the Influence of Excess of either Hydrogen or Oxygen respectively on the Rate of Combination.

The primary object of these experiments was to test the validity of the "diffusion" theory. If the observed rate of change in a heterogeneous gas system is determined by diffusion factors only, it must, at any given moment, depend on the rate at which the gas in defect at the surface diffuses on to it from the outside inert atmosphere.

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* That the combination was entirely a surface phenomenon was proved by a "blank" experiment in which the catalysing material was removed and normal electrolytic gas continuously circulated at a pressure of 478 millims. through the empty combustion tube at 430° for 6 hours. There was, however, no fall in pressure. This blank experiment, therefore, shows also that the glass surface of the combustion tube had no appreciable influence at 430° on the course of events.

† [*Added February* 10, 1906.—Since nothing but steam was produced in the above experiments, this analysis proves that the gas obtained by the electrolysis of a solution of pure barium hydroxide contains hydrogen and oxygen in exactly equivalent proportions.]

Now since the rate of diffusion of hydrogen is four times that of oxygen, it follows, assuming the rate of combination at the surface to be infinite, that with normal electrolytic gas there will always be an excess of hydrogen at the surface. The rate of steam formation would, therefore, be determined by the rate of diffusion of the oxygen. This conclusion is obviously not incompatible with the results of the previous experiments with the normal gas. Applying the same argument to cases in which the gases are not present in their combining proportions, it follows that so long as the hydrogen exceeds one-third of the total volume its rate of diffusion will maintain it in excess at the surface, and the rate of steam formation should depend on the partial pressure of the oxygen only. As soon, however, as the hydrogen falls below this limit, the rate should depend on the partial pressure of the hydrogen only.

In tabulating the results of these experiments it will be necessary to record in separate columns the partial pressures of both hydrogen and oxygen, as well as the constants calculated from each set of partial pressures. In this way the influence of each gas on the rate of change can be seen at a glance. In the following tables, therefore :—

t = time in hours from the beginning.

P = total pressure of the dry gas (corr.) in the apparatus.

P_{H_2} = the partial pressure of the hydrogen.

P_{O_2} = the partial pressure of the oxygen.

$$k_{H_2} = \frac{1}{t} \log \frac{P_{0H_2}}{P_{tH_2}}.$$

$$k_{O_2} = \frac{1}{t} \log \frac{P_{0O_2}}{P_{tO_2}}.$$

T = temperature of the combustion tube.

EXPERIMENT V.

March 21, 1904.

Original mixture = $3H_2+O_2$ nearly. The rate of circulation was rapid, and [32·5 per cent. of the original oxygen disappeared during the first two hours.—*February* 10, 1906.] T = 430°.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	411·8	311·8	100·0	—	—
2	314·2	246·7	67·5	0·0509	0·0853
4	243·4	199·5	43·9	0·0485	0·0894
6	184·9	160·5	24·4	0·0481	0·1021
8	144·2	133·4	10·8	0·0461	0·1208
10	117·4	115·5	1·9	0·0431	0·1721

In a comparative experiment (VI.) made, three days later, with normal electrolytic gas, under precisely the same conditions, [only 21·5 per cent. of the oxygen initially present disappeared during the first two hours, the values of "k_1" varying between 0·0572 and 0·0532 as the pressure in the apparatus fell from 429·6 to 116·6 millims. in 12 hours.—*February* 10, 1906.]

These two experiments bring to light the significant fact that where an excess of hydrogen is initially present, the rate of combination does not depend on the partial pressure of the oxygen, as the diffusion theory demands, but rather on that of the hydrogen. The increasing excess of hydrogen in Experiment V. steadily accelerated the disappearance of the oxygen.

In the next three experiments (VII. to IX. inclusive), the influence of rather a large excess of hydrogen or oxygen respectively on the initial rate of change was studied. The rate of circulation was the same in all three experiments, but it was purposely made slower than in the two preceding experiments, in order that the reaction might be extended over 8 or 10 hours in each case. In Experiment VII. (April 7, 1904), the mean value of the reaction constant "k_1" for normal electrolytic gas was found to be 0·0195.

In Experiments VIII. and IX., original mixtures corresponding nearly to $9H_2+O_2$ and H_2+6O_2, respectively, were employed, with the following results:—

EXPERIMENT VIII. April 8, 1904. Original mixture = $9H_2+O_2$ nearly. T = 430°.					EXPERIMENT IX. April 15, 1904. Original mixture = H_2+6O_2 nearly. T = 430°.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	377·9	41·9	—	—	0	48·7	296·3	—	—
2	351·1	28·5	0·0159	0·0837	2	44·1	294·6	0·0216	0·0018
4	328·5	12·2	0·0152	0·0960	4	39·7	291·8	0·0222	0·0017
6	311·1	8·5	0·0141	0·1154	6	35·5	289·7	0·0229	0·0016
8	297·7	1·8	0·0129	0·1708	12	26·7	285·3	0·0217	0·0014
					18	19·6	281·8	0·0218	0·0012
					24	12·9	278·5	0·0240	0·0011

The rates of change observed in the three experiments may be best compared by considering the percentage of the original electrolytic gas which disappeared during the first two hours in each case. In Experiments VII. and IX., with "normal" gas and excess of oxygen respectively, these percentages were practically the same, namely, 9·1 and 9·4 respectively. The corresponding figure in Experiment VIII., however, with excess of hydrogen, was no less than 32 per cent., a very clear proof of the accelerating influence of excess of hydrogen.

The conclusion that the rate of change is proportional to the partial pressure of the hydrogen, was finally confirmed by the two following experiments, in which the original mixtures corresponded to approximately H_2+O_2 and $3H_2+O_2$ respectively. The rate of circulation, which was the same in both, was somewhat faster than in the three preceding experiments (VII. to IX.).

Experiment X.

April 26, 1904.
Original mixture = H_2+O_2. T = 430°.

t.	P.	p_{H_2}.	p_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	398·0	196·0	202·0	—	—
2	358·0	169·2	188·8	0·0320	0·0148
4	329·5	150·2	179·3	0·0289	0·0130
6	294·0	126·5	167·5	0·0317	0·0136
8	268·4	109·5	158·9	0·0316	0·0131
12	228·3	82·7	145·6	0·0312	0·0119
24	156·9	35·1	121·8	0·0311	0·0092
28	142·1	25·3	116·8	0·0318	0·0085
32	129·0	16·5	112·5	0·0335	0·0080

Experiment XI.

April 29, 1904.
Original mixture = $3H_2+O_2$. T = 430°.

t.	P.	p_{H_2}.	p_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	387·4	292·5	94·9	—	—
2	339·4	260·5	78·9	0·0253	0·0401
4	294·4	230·5	63·9	0·0259	0·0429
6	258·0	206·2	51·8	0·0253	0·0438
8	227·6	185·9	41·7	0·0246	0·0447
10	200·4	167·8	32·6	0·0241	0·0464
12	176·4	151·8	24·6	0·0237	0·0488
14	154·4	137·1	17·3	0·0235	0·0528
16	134·0	123·6	10·4	0·0240	0·0600
18	115·8	111·4	4·4	0·0233	0·0741

3rd Group.—Experiments Showing the Stimulating Influence of Hydrogen upon the Catalysing Power of the Surface.

The fact that the rate of combination throughout a given experiment is always proportional to the partial pressure of the hydrogen, can hardly have any other meaning than that the formation of steam is an indirect process, dependent on a primary change, induced by the surface, in which the hydrogen is concerned. This led us to investigate the separate influence of hydrogen and oxygen respectively at 430°, and also of hydrogen at red heat, upon the catalysing power of the surface.

At 430°.

The general plan of this series of seven experiments (XII. to XVIII. inclusive), all made with normal electrolytic gas at 430°, under precisely the same conditions as regards rate of circulation, was briefly the following :—

Before each experiment (except the first, which was simply made to determine the "normal" value of the reaction constant "k_1" for the series), either hydrogen or oxygen was circulated over the surface at 430° for a period of time varying from 24 to 72 hours. The gas was then rapidly withdrawn from the apparatus by means of the auxiliary Sprengel pump, the action of which was continued for about 15 or 20 minutes after the manometer had indicated a "moist" vacuum. A charge of electrolytic gas was immediately admitted, and the rate of combination determined over a period of 8 or 10 hours in the usual manner. Finally, the apparatus was again thoroughly exhausted. The furnace was never turned down during the whole of the five weeks over which the series of experiments extended, and the apparatus was kept exhausted during the intervals between each experiment. The rate of circulation in each experiment was 1 in 35 minutes.

Experiment XII.—In this experiment, in which electrolytic gas was admitted to the apparatus without any preliminary treatment of the surface with either hydrogen or oxygen, the mean value for "k_1" was found to be 0·0363.

In two of the three following experiments (namely, XIII. and XV.), the surface was subjected to a preliminary treatment with hydrogen at 430° for 24 and 40 hours respectively, and in the third (XIV.) to the action of oxygen for 24 hours. The results are tabulated below :—

EXPERIMENT XIII. May 3 and 4, 1904. Preliminary treatment with hydrogen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			EXPERIMENT XIV. May 7 and 8, 1904. Preliminary treatment with oxygen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			EXPERIMENT XV. May 9 to 11, 1904. Preliminary treatment with hydrogen at 430° for 40 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t.	P.	k_1.	*t.*	P.	k_1.	*t.*	P	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	397·4	—	0	388·4	—	0	347·9	—
2	313·5	0·0515	2	337·6	0·0305	2	264·8	0·0592
4	252·5	0·0492	4	297·0	0·0291	4	203·5	0·0582
6	211·4	0·0457	6	257·5	0·0291	6	155·1	0·0584
8	177·4	0·0438	8	228·0	0·0287	8	120·8	0·0578
10	149·4	0·0425				10	89·0	0·0592

The catalysing power of the surface was, therefore, greatly stimulated by previous exposure to hydrogen at 430°, the stimulus being the more marked and enduring the longer the surface had been subjected to the action of the gas. Moreover, the great contrast between the rates observed, according as the surface had been previously treated with hydrogen or oxygen, is very striking. The stimulus imparted by the 40 hours' preliminary treatment with hydrogen in Experiment XV. gradually wore away when successive charges of electrolytic gas were circulated over the surface, until finally it was restored to its normal condition.

In the next three experiments (XVI. to XVIII. inclusive), the stimulating influence of hydrogen was very marked. In Experiment XVI., after a preliminary treatment of the surface with oxygen at 430° for 48 hours, the rate of combination observed was almost exactly normal (compare Experiment XII.). In Experiment XVIII., the usual procedure was somewhat modified in that after the 24 hours' preliminary treatment with hydrogen the apparatus was continuously exhausted for 18 hours, the combustion tube being kept at 430° the whole time. It is evident from the results that the imparted "stimulus" survived this long exhaustion.

Experiment XVI.			Experiment XVII.			Experiment XVIII.		
May 12 to 14, 1904. Preliminary treatment with oxygen at 430° for 48 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			May 16 to 19, 1904. Preliminary treatment with hydrogen at 430° for 72 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			May 30 to 31, 1904. Preliminary treatment with hydrogen at 430° for 24 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t.	P.	k_1.	t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	412·7	—	0	405·2	—	0	298·8	—
2	347·5	0·0373	2	304·3	0·0622	2	233·8	0·0543
4	289·5	0·0385	4	225·4	0·0637	4	181·3	0·0542
6	244·0	0·0380	6	175·8	0·0604			
8	208·7	0·0370	8	138·0	0·0585			

The ratio hydrogen/oxygen in the gas withdrawn from the apparatus at the end of Experiment XVII. was 2·138, a circumstance which certainly indicates some occlusion of hydrogen in the pores of the porcelain during the long preliminary treatment. The stimulus caused by the hydrogen in this experiment gradually wore away as successive charges of electrolytic gas were circulated over the surface during the next 18 hours, until finally it was restored to its normal condition.

At Red Heat.

Whilst the preceding experiments leave no room for doubt but that the catalytic action of porcelain is connected with a preliminary change in which the hydrogen is chiefly concerned, they do not discriminate between a chemical and a physical explanation of the process. If the stimulating effect of hydrogen at 430° is due to a chemical reduction of the catalysing material, we should expect a greatly enhanced and more permanent effect after long treatment with hydrogen at red heat. But, on the other hand, if the stimulus in question is due to a physical change in the hydrogen within the cavities of the material, subsequent long exhaustion at red heat should materially diminish, if not entirely obliterate it. This was the issue we attempted to decide in the next two experiments, which were carried out in the following manner:—

Before each experiment the combustion tube containing the porcelain was transferred to an ordinary combustion furnace and connected, through fused glass joints, at the one end with a supply of pure dry hydrogen, and at the other end with a Sprengel pump and manometer. The tube was heated to bright redness in a slow current of hydrogen for from 36 to 48 hours, and subsequently exhausted at dull red heat for 20 hours. The stop-cocks at each end of the tube were then closed, and it was transferred back again to the circulation apparatus, when the rate of combination for normal electrolytic gas at 430° was once more determined, the rate of circulation being precisely the same as in the preceding experiments of the series. The results of the two experiments are tabulated below:—

Experiment XIX.			Experiment XX.		
June 3 to 6, 1904. Preliminary treatment with hydrogen at red heat for 48 hours, followed by exhaustion at red heat for 20 hours. Rate of circulation = 1 in 35 minutes. T = 430°.			June 8 to 11, 1904. Preliminary treatment with hydrogen at red heat for 36 hours, followed by exhaustion at red heat for 12 hours. Rate of circulation = 1 in 35 minutes. T = 430°.		
t	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	398·8	—	0	383·6	—
1	364·9	0·0386	2	325·6	0·0356
2	336·8	0·0368	4	283·3	0·0329
3	311·3	0·0359	6	243·2	0·0330
6	246·1	0·0349	10	179·2	0·0330
7	225·0	0·0355	12	154·2	0·0330

These rates show very decisively that the surface had not been stimulated by the long exposure to hydrogen at red heat. The values of "k_1" are practically the same as the value obtained in Experiment XII., namely 0·0363, with the surface in a "normal" condition, and with the same rate of circulation. Hence the peculiar action of hydrogen in the catalytic process cannot be ascribed to a chemical reduction of the surface.

Absorption of Hydrogen by Porous Porcelain at Red Heat.

It was now necessary to ascertain whether or not hydrogen is occluded to any appreciable extent by porous porcelain at high temperatures. The combustion tube containing material used in the preceding experiments was transferred to the "absorption apparatus" (see Diagram I., fig. 2), where, after a preliminary thorough exhaustion at 700°, pure hydrogen, which had been just previously passed over red hot copper, was admitted, and the subsequent absorption of the gas by the red hot porcelain was followed by pressure readings at frequent time intervals. In three different experiments the following records were obtained :—

t	0	1	2	3	4	5	10	15	20	30	60 minutes
(1) P . . .	720	664	645	636	628	621	597	585	575	561	532 millims.
(2) P . . .	740	—	688	677	—	668	646	637	630	621	— ,,
(3) P . . .	766	706	693	686	680	674	665	657	650	633	— ,,

The gas absorbed at red heat was very obstinately retained when the apparatus was exhausted at the ordinary temperature. In the third of the above experiments, for instance, it was not removed after 10 hours' continuous pumping. As soon, however, as the tube was again heated to redness, the occluded gas could always be completely removed after two or three hours' pumping.

3rd, 4th and 5th Series.—Experiments with Surfaces C, D and E.

Whilst the behaviour of these three surfaces resembled that of the surface B in the three important respects already referred to on pp. 13 and 14, certain differences were observed which must not be overlooked in constructing a theory of the catalytic process.

Surface C.

The activity of this surface was stimulated by long exposure to hydrogen at the ordinary temperature, but not when the treatment was repeated at 450°. The stimulating influence of hydrogen at the ordinary temperature is illustrated by the results of the following series of experiments, at 430°, with normal electrolytic gas :—

Normal electrolytic gas. T = 430°. Rate of circulation = 1 in 45 minutes.

Experiment.	Date.	Condition of surface.	k_1 for time interval 0 to 2 hours.
XXI.	February 17, 1905	Normal	0·0175
XXII.	„ 19, 1905	„	0·0165
XXIII.	March, 1, 1905	After exposure to hydrogen in the cold for one week	0·0299
XXIV.	„ 3, 1905	After two days' exhaustion at 430°	0·0201
XXV.	„ 4, 1905	Normal	0·0170
XXVI.	„ 14, 1905	After exposure to hydrogen in the cold for ten days	0·0328

Another interesting feature about the behaviour of this surface was that in every experiment with mixtures containing an excess of oxygen, the activity was initially rapidly stimulated up to a fairly high limit, after which the rate of combination depended on the partial pressure of the hydrogen only. But whilst this enhanced activity was undoubtedly due to the excess of oxygen, it ceased as soon as all the hydrogen had disappeared. In other words, the surface was not stimulated under the influence of oxygen alone, either at 450° or at dull red heat, but only by an excess of oxygen in presence of hydrogen, and whilst the gases were actually combining. This peculiarity is well illustrated by the results of the following series of experiments at 450°:—

(*a*) With normal electrolytic gas :—

T = 450°. Rate of circulation = 1 in 60 minutes.

Experiment XXVII.	Surface normally active	$k_1 = 0\cdot0250$
,, XXVIII.	Surface after exposure to hydrogen at 450°	$k_1 = 0\cdot0220$
,, XXIX.	,, ,, oxygen ,,	$k_1 = 0\cdot0218$

(*b*) With mixtures originally corresponding to $3H_2+O_2$ and H_2+4O_2 respectively :—

EXPERIMENT XXX. June 2, 1905. Original mixture = $3H_2+O_2$. T = 450°. Rate of circulation = 1 in 60 minutes.					EXPERIMENT XXXI. June 20, 1905. Original mixture = H_2+4O_2. T = 450°. Rate of circulation = 1 in 60 minutes.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	*t*.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	370·7	123·1	—	—	0	99·3	397·4	—	—
1	357·4	116·4	0·0168	0·0242	2	81·5	389·0	0·0428	0·0046
2	343·6	109·6	0·0164	0·0252	4	66·5	381·5	0·0435	0·0044
4	315·6	95·6	0·0174	0·0274	6	54·6	375·7	0·0432	0·0041
6	293·8	84·7	0·0168	0·0271	8	44·6	370·7	0·0434	0·0038
8	271·3	73·4	0·0169	0·0281	10	36·4	366·6	0·0436	0·0035
12	235·2	55·3	0·0165	0·0289	18	16·5	356·8	0·0433	0·0026
16	207·2	41·3	0·0158	0·0296	22	11·9	353·7	0·0420	0·0023
20	184·0	29·8	0·0152	0·0308	26	7·5	351·5	0·0431	0·0021

The surface had the power of occluding hydrogen (but not oxygen) at dull red heat. In one experiment with pure hydrogen, carried out at 650° in the absorption apparatus, the pressure fell from 704 to 594 millims. during 30 minutes; this represented the occlusion of between 6 and 7 cub. centims. of gas, measured at 0° and 760 millims.

The results of the fourth series of experiments with surface D merely confirmed those obtained with C, and need not, therefore, be further described.

Surface E.

This surface had been previously used for experiments on the slow combustion of acetylene, and in its raw condition displayed a peculiar susceptibility to the stimulating influence of oxygen. Indeed, its activity was affected by previous exposure to hydrogen or oxygen at 450° in exactly the opposite sense to that observed with the surface B. This is shown by the results of the following series of experiments with normal electrolytic gas at 450°. The rate of circulation was 1 in 60 minutes throughout.

Experiment.	Date.	Condition of surface.	k_1 for time interval 0 to 1 hour.	Remarks.
XXXIV.	June 24, 1905	Normal	0·0636	Rate of combination proportional to pressure throughout each experiment.
XXXV.	,, 25, 1905	,,	0·0636	
XXXVII.	,, 27, 1905	After exposure to hydrogen at 454° for fourteen hours	0·0382	
XXXVIII.	,, 29, 1905	After two days' continuous exhaustion. Normal	0·0612	
XL.	July 1, 1905	After exposure to oxygen at 450° for sixteen hours	0·0879	Stimulus rapidly wore off. Surface again normal after five hours.
XLI.	,, 2, 1905	After further exposure to oxygen at 450°	0·0976	

In experiments with an excess of either of the two reacting gases, the surface was always more than normally active, and, after an initial period of acceleration, the rate of combination always remained proportional to the partial pressure of the hydrogen. This is shown by the results of the two following experiments with mixtures originally corresponding to $3H_2+O_2$, and H_2+3O_2, respectively. In the latter case, the rate of combination after the first hour was about 2·5 times normal, and the results are best analysed by calculating two sets of values for "k_{H_2}," the one set for the whole experiment, the other for the course of events after the first hour.

EXPERIMENT XXXVI.

June 26, 1905.
Original mixture = $3H_2+O_2$. T = 450°.
Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	380·4	130·7	—	—
2	304·3	92·6	0·0485	0·0748
3	269·1	75·0	0·0501	0·0804
4	239·7	60·3	0·0501	0·0840
5	215·1	48·0	0·0495	0·0870
6	190·7	35·8	0·0500	0·0937
7	169·1	25·0	0·0503	0·1026
9	134·5	7·7	0·0502	0·1366

EXPERIMENT XXXIX.

June 30, 1905.
Original mixture = H_2+3O_2. T = 450°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.		k_{O_2}.
hours.	millims.	millims.			
0	131·0	391·3	—	—	—
1	107·0	379·3	0·0779	—	0·0136
2	70·5	361·1	0·1345	0·181	0·0174
3	48·1	349·9	0·1450	0·174	0·0162
4	31·5	341·5	0·1547	0·177	0·0148
5	21·9	336·7	0·1554	0·172	0·0131
6	15·5	333·5	0·1545	0·168	0·0116
7	11·0	331·3	0·1504	0·165	0·0104

After the above experiments were concluded, the combustion tube containing the catalysing material was transferred to the "absorption apparatus," where its power of occluding hydrogen at dull red heat (*circa* 650°) was tested. In one experiment the pressure fell from 764 to 648 millims., and in another from 765 to 657 millims., or by about one-seventh, during 30 minutes. Corresponding experiments with oxygen gave negative results.

The catalysing power of the surface, as well as its susceptibility to any stimulus by oxygen, underwent a marked alteration as the result of the repeated occlusions of hydrogen, followed by prolonged exhaustion, at dull red heat. Its activity was now much reduced, the new "normal" value for "k_1" at 450° being only 0·033 as compared with the 0·063 obtained in previous experiments. It is, however, significant that the new value was almost identical with that obtained in Experiment XXXVII., namely, 0·0382, after the surface had been exposed to hydrogen at 450°.

In its new condition of reduced activity, the surface had completely lost its susceptibility to stimulus by oxygen; indeed, prolonged exposure to oxygen at 450° now actually diminished its catalysing power. On the other hand, it had acquired the power of responding, to a slight degree, to the stimulating influence of hydrogen at 450°. In short, its behaviour now approximated to that of surface B, a circumstance which proves how profoundly the action of porcelain may be affected by its past history.

Summary.

Reviewing now the results obtained with the five surfaces as a whole, it is clear that the rate of steam formation is governed neither by the "order" of the reaction, as Bodenstein asserted, nor by diffusion factors simply, as Nernst has suggested. Nor is the theory of a rapidly alternating series of oxidations and reductions of the catalysing surface admissible. The evidence is, on the contrary, altogether in favour of the view that the catalytic action of porcelain is primarily due to the condensation, or occlusion, of one, and possibly both, of the reacting gases on its surface. The fact that whenever one or other of the gases is present in excess, the rate of combination is proportional to the partial pressure of the hydrogen, and that the material absorbs hydrogen at red heat, indicates that occluded hydrogen is an all important factor in the process. It would also seem, from the results obtained with surfaces C and E, that occluded oxygen also may exercise an accelerating influence on the process; otherwise it is difficult to account for the fact that in several of the experiments with an excess of oxygen a surface proved more than normally active, and that surface E, before it had been subjected to the treatment with hydrogen at red heat, could be stimulated by previous exposure to oxygen at 450°. Another significant circumstance is that, whilst excess of hydrogen always produced a *continuous* acceleration throughout a given experiment, any acceleration due to an excess of oxygen was only manifested during the initial stages. These facts suggest the following view of the catalytic process. Porous porcelain occludes, or condenses, both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. In general, however, whereas in the case of oxygen the process is extremely rapid and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen.

PART II.—EXPERIMENTS WITH A BASIC SURFACE OF CALCINED MAGNESITE.

The primary object of these experiments was to ascertain whether a surface composed of basic and non-reducible oxides behaves in the same way towards electrolytic gas as does the acidic porcelain. The material selected was a specimen of magnesite containing considerably less than 1 part of iron in 100,000; it was thoroughly calcined at 1000° in a muffle furnace, and then packed into the combustion tube of the circulation apparatus.* The packed tube was heated to dull redness in a current of dry air for several hours; it was then cooled, and connected with the circulation apparatus, where it was thoroughly exhausted at 430° for 24 hours.

Several successive charges of normal electrolytic gas were then circulated in the apparatus, during which the catalysing power of the surface gradually increased up to a steady maximum, after which it remained practically constant. This steady state was regarded as the "normal" condition of the surface.

The following series of nine experiments was then made under precisely the same conditions as regards temperature (430°) and rate of circulation (namely, 1 in 60 minutes). In the first experiment, the rate of combination for normal electrolytic gas was shown to be directly proportional to the pressure of dry gas. In the second, where a mixture of approximately $3H_2+O_2$ was employed, it was found to be nearly proportional to the partial pressure of hydrogen.

After Experiment II., hydrogen was circulated over the surface at 430° for 16 hours, and on redetermining the rate of combination for normal electrolytic gas over the "hydrogenised" surface in Experiment III., it was found to be abnormally high. At the conclusion of Experiment III., the apparatus was exhausted at 430° for 16 hours, and on subsequently circulating a fresh charge of electrolytic gas over the surface, it was finally restored to its normal condition (Experiment IV.). The results of these four experiments are tabulated below :—

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* The calcined material had the following percentage composition :—$MgO = 87 \cdot 00$, $CaO = 12 \cdot 42$, $Al_2O_3 = 0 \cdot 33$, $SiO_2 = 0 \cdot 25$.

EXPERIMENT I.

July 6, 1904.
Normal electrolytic gas. Surface in "normal" condition.

t.	P.	k_1.
hours.	millims.	
0	369·8	—
1	268·8	0·1386
2	206·3	0·1268
3	151·0	0·1296
4	110·5	0·1312
5	77·8	0·1354
6	52·6	0·1413
8	25·2	0·1458

EXPERIMENT II.

July 7, 1904.
Original mixture $3H_2+O_2$ nearly.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	252·3	85·9	—	—
1	200·5	60·0	0·0997	0·1558
2	165·4	42·5	0·0917	0·1528
3	136·0	27·8	0·0895	0·1633
4	110·8	15·1	0·0894	0·1890
5	94·2	6·8	0·0856	0·2203
$5\frac{1}{2}$	87·5	3·5	0·0836	0·2527
6	83·3	1·4	0·0802	0·2980

EXPERIMENT III.

July 8, 1904.
Normal electrolytic gas over "hydrogenised" surface.

t.	P.	k_1.
hours.	millims.	
0	425·8	—
1	267·2	0·2024
2	150·2	0·2262
3	79·8	0·2424
4	36·7	0·2661
5	14·2	0·2954

EXPERIMENT IV.

July 9, 1904.
Normal electrolytic gas after prolonged exhaustion at 430°.

t.	P.	k_1
hours.	millims.	
0	390·0	—
1	257·2	0·1809
2	178·0	0·1704
3	125·8	0·1638
4	91·3	0·1576

The ratio H_2/O_2 in the residual gas from Experiment I. was exactly 2·0. For the residual gas in Experiment III. the ratio was, however, 2·2, a clear indication that hydrogen had been occluded by the catalysing material during the treatment to which it had been subjected between Experiments II. and III.

At the conclusion of Experiment IV., oxygen was circulated over the surface at 430° for 36 hours in order to completely "dehydrogenise" it. After pumping the residual oxygen out of the apparatus, the rate for normal electrolytic gas was now found to be very little more than half the normal value, as follows :—

EXPERIMENT V.

July 11, 1904.

Normal electrolytic gas after oxygen. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	400·0	—	6	147·6	0·0723
1	340·0	0·0706	7	123·2	0·0731
3	248·8	0·0687	8	103·2	0·0735
4	205·8	0·0721	9	86·0	0·0740
5	180·8	0·0690			

The pressure curves for Experiments I., II., and V., which are reproduced in Diagram III., show very clearly the effects of "hydrogenation" and "dehydrogenation" respectively on the activity of the surface.

The results of the last four experiments of the series may be discussed together. Starting with the surface in the condition in which it had been left after Experiment V., a mixture originally containing an excess of hydrogen ($3H_2+O_2$) was circulated over it (Experiment VI.). Its activity was at once stimulated, and the rate of steam formation as the experiment proceeded was always as nearly as possible proportional to the partial pressure of the hydrogen. The residual hydrogen from VI. was circulated over the surface at 430° for 16 hours. It was then pumped out of the apparatus, and, on redetermining the rate for normal electrolytic gas over the "hydrogenised" surface (Experiment VII.), it was found to be so abnormally active that no less than 41·67 per cent. of the original electrolytic gas disappeared during the first hour, and, moreover, the stimulus outlasted the four hours over which the experiment extended.

At the conclusion of Experiment VII., the combustion tube of the apparatus was transferred to a high temperature furnace and exhausted at dull red heat for 16 hours, during which all the hydrogen occluded by the catalysing material was extracted. The tube was then cooled and refitted into the circulation apparatus. The rate for normal electrolytic gas was afterwards redetermined (Experiment VIII.). The values of "k_1" now showed that the stimulus imparted by the hydrogen had practically disappeared, the material being in the same "normal" condition as in Experiment I. Clearly, therefore, the enhanced activity of the surface after exposure to hydrogen at 430° in Experiment III. cannot be attributed to any chemical reduction of the material composing it.

Finally, in Experiment IX., a mixture containing excess of oxygen was circulated over the surface. The rate of combination observed was strictly proportional to the partial pressure of the hydrogen throughout, and the values "k_{H_2}" showed that the surface was no more than normally active. The results of the four experiments are tabulated on the next page.

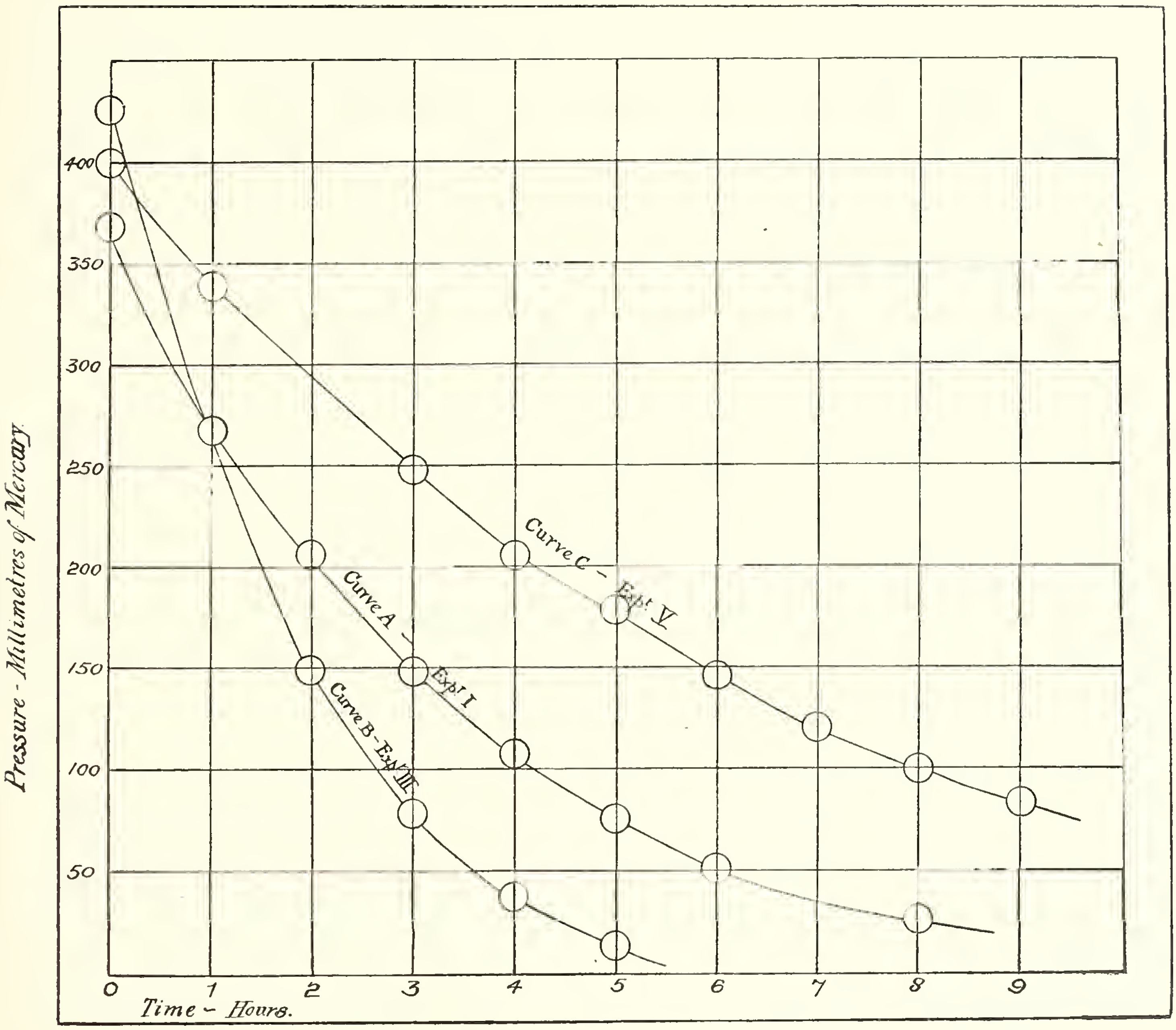

Diagram III. Experiments with magnesia. Pressure curves for normal electrolytic gas.

Curve A. Surface in "normal" condition.
,, B. "Hydrogenised" surface.
,, C. Surface "dehydrogenised" by exposure to oxygen.

Experiment VI.

July 15, 1904.
Original mixture $3H_2+O_2$ nearly. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	299·4	99·5	—	—
1	260·8	80·2	0·0600	0·0936
2	220·1	59·8	0·0663	0·1105
3	184·9	42·2	0·0698	0·1242
4	157·1	28·3	0·0700	0·1365
5	126·7	13·1	0·0747	0·1761
7	102·1	0·8	0·0668	0·2992

Experiment VII.

July 16, 1904.
Normal electrolytic gas over the "hydrogenised" surface. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	395·3	—
1	230·7	0·2339
2	138·4	0·2278
3	80·3	0·2307
4	46·3	0·2328

Experiment VIII.

July 27, 1904.
Normal electrolytic gas. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	401·2	—
1	291·3	0·1390
2	210·4	0·1402
3	151·4	0·1411
4	109·6	0·1408
5	78·6	0·1416

Experiment IX.

July 29, 1904.
Original mixture H_2+O_2. T = 430°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	134·1	266·5	—	—
1	97·9	248·4	0·1366	0·0305
2	71·3	235·1	0·1371	0·0272
3	52·8	225·9	0·1349	0·0239
4	37·6	218·2	0·1380	0·0217
6	18·8	208·9	0·1422	0·0176
8	10·3	204·6	0·1395	0·0143
10	5·3	202·1	0·1403	0·0120

Absorption of Hydrogen at Red Heat.

That the basic material had the power of absorbing hydrogen at red heat was proved by transferring the combustion tube containing it to the "absorption apparatus." The tube was exhausted at red heat until no more gas could be withdrawn from it. Pure hydrogen was then admitted up to 763 millims. pressure. The gradual absorption of the gas is shown by the following pressure records:—

t	0	1	2	5	10	20	30 minutes
P. . . .	763	744	738	719	706	691	682 millims.

The apparatus was then cooled and thoroughly exhausted at the ordinary temperature. It was again heated to redness, when about 5 cub. centims. of hydrogen were extracted. Experiments on the absorption of oxygen at red heat gave entirely negative results.

Summarising now the above results, it is evident that (1) with normal electrolytic gas the rate of combination is proportional to the pressure of the dry gas, (2) when an excess of either of the reacting gases is present, the rate is determined mainly by the partial pressure of the hydrogen, and (3) the catalysing power of the material is, on the one hand, greatly stimulated by hydrogen, but, on the other hand, diminished by oxygen. These considerations, together with the fact that the material occludes hydrogen but not oxygen at red heat, show that its catalytic action must be referred to its power of occluding hydrogen.

Part III.—Experiments with Silver.

In selecting silver as the first metallic surface for investigation, we had in view two considerations, namely (1) the instability of its oxides above 350°,[*] and (2) its relationship to sodium and copper, which suggest the possibility of its forming a hydride at high temperatures.[†] For most of the experiments, the metal was employed in the form of a gauze of 23 strands per centimetre, each strand having a diameter of 0·18 millim.;[‡] a final series of experiments was, however, made with foil prepared from "assay" silver.

First Series with Silver Gauze at 400°.

Throughout the first series of six experiments, the temperature of the combustion tube was 400°, and the rate of circulation 1 in 60 minutes. The weight of silver gauze employed was 62 grammes, and the area exposed to the reacting gases would be about 430 sq. centims.

At the outset of the series, successive charges of normal electrolytic gas were continuously circulated over the heated gauze for 12 hours, its catalysing power gradually increased, by about 30 per cent., up to a steady maximum, which was considered to represent the "normal" condition. The rate of combination was then determined as follows:—

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[*] According to Carnelly and Walker ('Trans. Chem. Soc.,' 1888, vol. 53, p. 79), the decomposition of Ag_2O, which is rapid between 270° and 300°, is quite complete between 300° and 430°.

[†] The recent experiments of Leduc ('Comp. Rend.,' 1902, vol. 135, p. 1332, and 1903, vol. 136, p. 1254) have shown that copper forms a stable hydride at temperatures below red heat, where the tension of dissociation only becomes appreciable at temperatures when the metal rapidly absorbs oxygen from the air.

[‡] The gauze, which was kindly supplied by Messrs. Johnson and Matthey, was made of the purest obtainable wire. We made a careful chemical analysis of about 10 grammes of the gauze, but were unable to detect the presence of any impurity. Both copper and bismuth were specially tested for.

Experiment I.

July 25, 1904.
Normal electrolytic gas. T = 400°. Surface in "normal" condition.
Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	447·5	—	4	115·8	0·1468
1	325·5	0·1381	5	82·4	0·1469
2	241·4	0·1341	6	58·5	0·1473
3	166·7	0·1429	7	41·4	0·1477

The values of "k_1," calculated from the expression $\frac{1}{t}\log\frac{C_0}{C_t}$, show that, as in the cases of porous porcelain and magnesia, the rate of steam formation is directly proportional to the pressure of the dry gas, and, therefore, that the process is a surface phenomenon entirely. In the next three experiments (II. to IV. inclusive), the influence of oxygen on the catalysing power of the surface was studied. In Experiment II., a mixture originally corresponding to H_2+2O_2 was employed, with the following results :—

Experiment II.

July 25, 1904.
Electrolytic gas + excess of oxygen. The original mixture corresponded to H_2+2O_2.
T = 400°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	130·7	261·4	—	—
1	103·5	248·0	0·1013	0·0228
2	82·1	237·1	0·1009	0·0212
3	60·7	226·5	0·1110	0·0207
4	44·9	218·6	0·1160	0·0194
5	28·9	210·5	0·1310	0·0188
$5\frac{1}{2}$	22·9	207·7	0·1376	0·0180
6	17·9	205·1	0·1439	0·0175
7	12·1	202·1	0·1476	0·0159
8	8·9	200·7	0·1458	0·0144
9	6·1	199·2	0·1478	0·0131

These numbers show that, initially, the rate of steam formation was proportionately rather slower than with normal gas in the previous experiment; it was, however, gradually accelerated as the experiment proceeded, until after the fourth hour it had attained a steady maximum. From this point onwards the rate remained nearly proportional to the partial pressure of the hydrogen. The significance of these results will be considered later.

At the conclusion of Experiment II., successive determinations were made of the rate for normal electrolytic gas (1) after the surface had been subjected to the action of oxygen at 450° for 36 hours, and (2) after the apparatus had been further exhausted during 12 hours. The results of these two experiments, which are tabulated below, show that oxygen *per se* has no stimulating influence on the activity of the surface, but rather, owing to its "dehydrogenising" action, the reverse. The long exhaustion which intervened between the two experiments completely restored the surface to its normal condition.

Experiment III. July 27, 1904. Normal electrolytic gas after treatment with oxygen 36 hours. T = 400°. Rate of circulation = 1 in 60 minutes.			Experiment IV. July 28, 1904. Normal electrolytic gas. Surface in "normal" condition. T = 400°. Rate of circulation = 1 in 60 minutes.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	470·4	—	0	467·3	—
1	357·4	0·1193	1	336·2	0·1430
2	256·6	0·1316	2	240·7	0·1441
3	167·8	0·1492	3	170·3	0·1462
4	112·6	0·1552	4	120·6	0·1471
5	71·2	0·1640			

The results of the last two experiments of the series (V. and VI.) are chiefly interesting in that they point to a theory of the catalytic process. Starting with the surface in the "normal" condition, a mixture containing an excess of hydrogen was admitted to the apparatus, and the rate of combination observed until nearly the whole of the oxygen had disappeared (Experiment V.). During the interval between Experiments V. and VI., hydrogen was circulated over the gauze at 400° for 18 hours and then pumped out of the apparatus. Immediately afterwards the rate for normal electrolytic gas over the "hydrogenised" surface was determined (Experiment VI.). The results of the two experiments are tabulated below :—

EXPERIMENT V. August 3, 1904. Original mixture = $3H_2 + O_2$ (nearly). T = 400°. Rate of circulation = 1 in 60 minutes.					EXPERIMENT VI. August 4, 1904. Normal electrolytic gas over "hydrogenised" surface. T = 400°. Rate of circulation = 1 in 60 minutes.		
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k.
hours.	millims.	millims.			hours.	millims.	
0	286·0	98·7	—	—	0	358·4	—
1	202·1	56·7	0·1508	0·2407	1	218·8	0·2143
$1\frac{1}{2}$	170·5	41·0	0·1498	0·2544	2	133·1	0·2151
2	145·2	28·3	0·1472	0·2712	3	78·4	0·2200
3	118·8	15·1	0·1272	0·2718	4	47·6	0·2192
$3\frac{1}{2}$	110·9	11·2	0·1176	0·2700	5	25·0	0·2313

The immediate effect of the excess of hydrogen in Experiment V. was a marked stimulation of the surface, which increased up to nearly the end of the second hour, when, it would appear, the surface had become fully hydrogenised. In conformity with this idea, the rate of steam formation was, during the interval 0 to 2 hours, nearly proportional to the partial pressure of the hydrogen; afterwards, however, it was largely governed by the oxygen pressure.

The stimulation of the surface by hydrogen is not only well marked, but is also shown to be very enduring, in Experiment VI.

Second Series with Silver Gauze at 400°.

At the outset of this series of experiments, the gauze was taken out of the combustion tube and heated to a temperature just short of the melting-point. A marked change took place both in its outward appearance and mechanical properties. The metal had lost its original elasticity and become exceedingly brittle; its surface had assumed a beautiful frosted appearance, and was covered with minute pits and excrescences, as will be seen from the photomicrograph B of it reproduced on p. 37. This should be compared with A, which shows the original condition of the surface. The whole behaviour of the metal suggested the breaking up of a hydride, and recalled the experiments of BEILBY and HENDERSON on the action of ammonia on metals at high temperatures.* In the case of silver, they found that "at 800° the polished surface of fine silver wire acquired a frosted appearance, and when examined with the microscope the wire was found to be coated all over with minute rounded blisters or bubbles, whilst there was very distinct evidence of 'spitting.' The elasticity of the metal was also very greatly reduced." They attributed the change to the rapid formation and decomposition of an unstable nitride. GRAHAM also noticed a very similar effect in his experiments on the occlusion of hydrogen by metals. He records that 108·8 grammes of silver wire occluded 0·211 vol. of hydrogen (2·2 cub. centims.) when heated to redness and slowly cooled in the gas, and that "the metal acquired a beautiful frosted appearance on the surface, and by repeated heating it became highly crystalline and brittle."*

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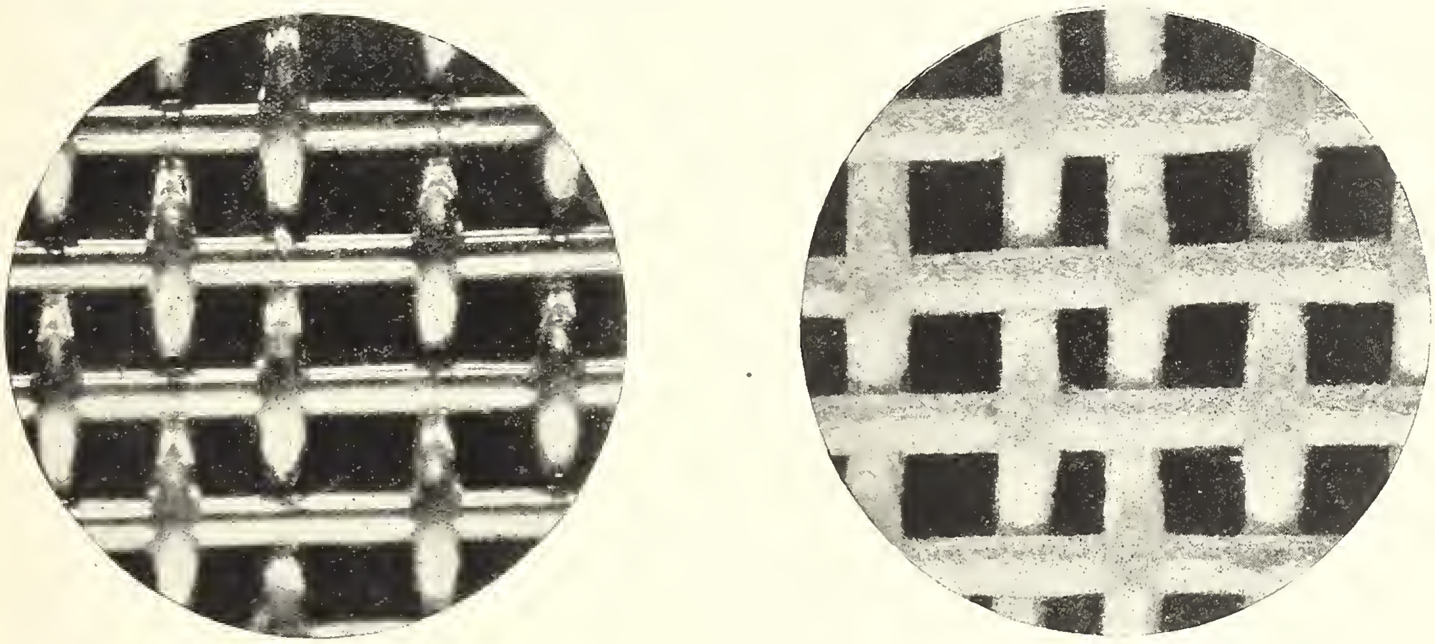
* 'Trans. Chem. Soc.,' 1901, vol. 79, p. 1245.



A. In its original condition.

B. After first series of experiments at 400° and subsequent heating (*vide* p. 36).

Photomicrographs of the silver gauze.

In view of the greatly increased surface area of the metal, consequent upon the treatment referred to above, we were not surprised to find that its catalysing power had increased something like threefold (as compared with the "normal" rate in the previous series), when the rate for normal electrolytic gas was re-determined (Experiment VII.), as under:—

EXPERIMENT VII.

September 11, 1904.
Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$ hours.
P	337·8	148·2	45·2	18·6 millims.
k_1	—	0·7154	0·8735	0·8394

That the enhanced catalysing power of the gauze was really due to its increased surface area was proved by rubbing off part of the frosted surface (it was obviously impossible to remove it in places where the strands of wire overlapped) with a chamois leather, and subsequently re-determining the rate of combination for normal gas in the two following experiments :—

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* 'Phil. Trans.,' 1866, vol. 156, p. 435; also 'Chemical and Physical Researches,' pp. 275–277.

EXPERIMENT VIII.

September 20, 1904.
Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.

t.	P.	k_1.
hours.	millims.	
0	397·6	—
$\frac{1}{2}$	246·6	0·4150
1	153·2	0·4142
$1\frac{1}{2}$	97·8	0·4062
2	58·6	0·4158
$2\frac{1}{2}$	36·8	0·4134
3	22·9	0·4132

EXPERIMENT IX.

September 21, 1904.
Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 65 minutes.

t.	P.	k_1
hours.	millims.	
0	367·4	—
$\frac{1}{2}$	222·9	0·4342
1	141·4	0·4148
$1\frac{1}{2}$	90·6	0·4054
2	55·0	0·4124
$2\frac{1}{2}$	33·8	0·4146
3	20·2	0·4199

In the next experiment, a mixture initially corresponding to $3H_2+O_2$, nearly, was employed. The residual hydrogen was subsequently circulated over the gauze at 400° for 16 hours, after which it was pumped out, and the rate for "normal" electrolytic gas re-determined (Experiment XI.).

EXPERIMENT X.

September 21, 1904.
Electrolytic gas plus excess of hydrogen, $3H_2+O_2$. T = 400°. Rate of circulation = 1 in 65 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	298·1	100·9	—	—
$\frac{1}{2}$	223·1	63·5	0·2516	0·4018
1	156·7	30·3	0·2792	0·5223
$1\frac{1}{2}$	129·1	16·4	0·2422	0·5260
2	114·9	9·2	0·2070	0·5199
$2\frac{1}{2}$	106·9	5·4	0·1781	0·5085

EXPERIMENT XI.

September 22, 1904.
Normal electrolytic gas over "hydrogenised" surface. T = 400°. Rate of circulation = 1 in 65 minutes.

t.	P.	k_1.
hours.	millims.	
0	370·4	—
$\frac{1}{2}$	158·2	0·7388
1	59·4	0·7949
$1\frac{1}{2}$	19·3	0·8554

The results of Experiment X. confirm those of the corresponding experiment of the previous series (Experiment V.) with the mixture $3H_2+O_2$. Up to a certain condition of maximum "hydrogenation," the rate of steam formation largely depended on the partial pressure of the hydrogen, afterwards, however, on that of the oxygen. In

Experiment XI. the further stimulation of the surface by hydrogen is again well marked. Moreover, it proved very enduring in character, hardly fading at all during several successive experiments with normal electrolytic gas, and, indeed, subsequent complete "dehydrogenation" of the surface by oxygen at 400° only reduced the value of "k_1" for normal electrolytic gas to 0·6554. It is evident, therefore, that the stimulating action of hydrogen was partly due to the surface becoming "hydrogenised," and partly also to the permanent increase in the surface area when this condition was removed. This was very clearly shown in the next two experiments (XII. and XIII.). Starting with the gauze in its completed "dehydrogenised" condition, hydrogen was again circulated over it at 400° for 16 hours, and afterwards rapidly withdrawn from the apparatus. The rate for normal electrolytic gas was at once re-determined, as follows:—

Experiment XII.

Normal electrolytic gas over "hydrogenised" gauze. T = 400°.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1 hour.
P	371·1	203·4	115·1	66·6	36·6 millims.
k_1	—	1·0488	1·0168	0·9944	1·006

The increase in the value of "k_1" from 0·65 to 1·04 must be ascribed to the direct influence of hydrogen, that is to say, to the association of hydrogen with the surface.

The combustion tube containing the gauze was now transferred to a high-temperature furnace and exhausted, first in the cold, and afterwards at red heat. About 9 cub. centims. of hydrogen were extracted during four hours at red heat, and the exhaustion was continued for a full hour after the gas had ceased to be evolved. The gauze was cooled *in vacuo*, and the tube afterwards transferred back to the circulation apparatus, where the rate for normal electrolytic gas was finally re-determined (Experiment XIII.). The complete removal of the hydrogen had left the gauze in an extremely "active" condition, owing to the large increase in its surface area and porosity.

Experiment XIII.

September 26, 1904.
Normal electrolytic gas. T = 400°.

t	0	$\frac{1}{4}$	$\frac{1}{2}$ hour.
P	327·6	36·6	2·6 millims.
k_1	—	3·80	4·20

The Absorption of Hydrogen by Silver.—At Dull Red Heat.

It now became necessary to obtain some further evidence concerning the absorption of hydrogen by silver at high temperatures. Accordingly the combustion tube (capacity = 135 cub. centims.) containing the 62 grammes of silver gauze employed in the preceding experiments was transferred to the "absorption" apparatus, where it was thoroughly exhausted at dull red heat (*circa* 650°) during several hours. Pure hydrogen was then admitted up to a pressure of 744 millims. A rapid absorption of the gas at once began, the pressure falling to 381 millims. in 25 minutes, as follows :—

t . .	0	2	4	6	8	10	15	20	25 minutes
P .	774	689	610	547	499	464	414	395	381 millims.

The tube was next allowed to cool, and was subsequently exhausted at the room temperature until the whole of the unabsorbed gas (about 25 cub. centims.) had been extracted. The temperature was thereupon again raised to dull red heat, and the exhaustion continued for 15 hours longer. During the whole of this time hydrogen was very slowly evolved (about 7·5 cub. centims. were collected within the first three hours), and a mirror of silver appeared near the cool end of the combustion tube, a circumstance which suggested the decomposition of a hydride rather than the mere giving off of "condensed" or "occluded" gas.

In order to completely "dehydrogenise" the surface, pure oxygen was now admitted to the red hot tube up to a pressure of 763 millims. During the next minute the pressure rapidly fell to 683 millims., and water condensed in the cool ends of the tube. There then followed a very slow fall in pressure (29 millims. during the next 14 minutes), probably due to a small absorption of oxygen. The pressure records during this treatment with oxygen were as follows :—

t . . .	0	1	2	3	4	5	10	15 minutes
P . . .	763	686	680	675·5	672	669	662·5	657 millims.
	H_2O formed							

The tube was next continuously exhausted at dull red heat for 14 hours, after which pure hydrogen was once more admitted up to a pressure of 747 millims. There followed a very rapid absorption, the pressure falling to 432 millims. within the first five minutes, and to 180 millims. by the end of an hour. During the first minute there was a slight condensation of moisture in the cool ends of the tube, due to the burning out of the small amount of residual occluded oxygen. The pressure records during the absorption of hydrogen were as follows :—

t	0	1	2	3	4	5	10	15	20	30	60	120	150 minutes.
P . . .	747	639	571	516	472	432	334	275	244	210	181	157	155 millims.
	some H_2O formed												

The tube was finally exhausted (1) at the room temperature for an hour for the removal of any unabsorbed gas, and (2) at dull red heat for 40 hours, during which no less than 26 cub. centims. of hydrogen were very slowly extracted.

[*Third Series with Silver Gauze at* 500°.

In a series of experiments with normal electrolytic gas at this temperature, it was proved that the rate of combination, although very fast, still remained proportional to the partial pressure, and that, as at 400°, the catalysing power of the surface was stimulated, in a marked degree, by previous exposure to hydrogen.—*January* 31, 1906.]

Fourth Series with Silver Foil at 400°.

In order to ascertain whether the catalytic process is materially influenced by the physical character of the surface, a final series of experiments was made at 400° with pure silver foil. A piece of pure "assay" silver was rolled out into a thin ribbon (40 centims. long and 1·5 centims. broad), and after its surface had been slightly etched by momentary immersion in cold dilute nitric acid, followed by a thorough washing with hot distilled water, it was wound spirally round a glass rod. The extremities of the rod were provided with small glass projections, so that it would rest inside the combustion tube of the circulation apparatus without the foil touching the glass walls. The area of the foil exposed to the reacting gases was 60 sq. centims.

Successive charges of normal electrolytic gas were circulated over the foil at 400°, until the rate of combination, which was at first rather slow, had attained a steady maximum. The values of "k_1" increased from 0·0310 to 0·0770 during this period, after which the rate of combination remained proportional to the pressure of the dry gas. This is shown in Experiment XXII., which gives the normal value of "k_1" for the series.

EXPERIMENT XXII.

April 7, 1905.
Normal electrolytic gas. T = 400°. Rate of circulation = 1 in 70 minutes.

t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	560·2	—	7	162·6	0·0767
1	468·3	0·0779	9	115·9	0·0760
2	388·1	0·0795	11	82·1	0·0758
3	325·1	0·0788	12	70·5	0·0750
5	234·2	0·0758	23	10·7	0·0747
6	194·0	0·0767			

In the next experiment (XXIII.), a mixture corresponding very nearly to $3H_2+O_2$ was employed. The surface was immediately stimulated, and the rate of charge was much more proportional to the partial pressure of the hydrogen than to that of the oxygen throughout the experiment. The results were as follows:—

EXPERIMENT XXIII.

April 8, 1905.
$3H_2+O_2$. T = 400°. Rate of circulation = 1 in 75 minutes.

t.	P.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.	millims.		
0	394·8	297·2	97·6	—	—
½	364·8	277·2	87·6	0·0606	0·0938
1	332·4	255·6	76·8	0·0656	0·1040
1½	298·0	232·6	64·5	0·0710	0·1158
2	266·3	211·4	54·9	0·0740	0·1249
2½	238·2	192·6	45·6	0·0754	0·1322
3½	189·9	160·4	29·5	0·0764	0·1484
4	171·0	147·8	23·2	0·0778	0·1562
4½	147·6	132·2	15·4	0·0782	0·1782

The residual hydrogen was then circulated over the foil at 400° for 22 hours, after which the apparatus was exhausted (1 hour), and a fresh charge of electrolytic gas admitted. The rate of combination observed (Experiment XXIV.) was extremely rapid, no less than 66·8 per cent. of the original gas disappearing within an hour as compared with only 16·5 per cent. in Experiment XXII., when the foil was in a condition of "normal" activity. The rapidly diminishing values of "k_1" indicated a fading away of the stimulus as the experiment proceeded. In order to completely "dehydrogenise" the foil, air was circulated over it at 400° for 22 hours. The apparatus was again exhausted, and finally the rate for normal electrolytic gas was re-determined in Experiment XXV. The results of this experiment prove that the "dehydrogenised" foil had become comparatively inactive; as the experiment proceeded, however, its catalysing power gradually increased, until finally it attained the "normal" value. The striking difference between the course of events in Experiments XXIV. and XXV. proves how completely the catalytic process depends on the association of the metal with hydrogen. The rate of circulation in these two experiments was 1 in 75 minutes.

Experiment XXIV. April 9, 1905. T = 400°. Normal electrolytic gas over "hydrogenised" foil.			Experiment XXV. April 11, 1905. T = 400°. Normal electrolytic gas over "dehydrogenised" foil.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	521·0	—	0	479·6	—
$\frac{1}{4}$	334·0	0·7776	$\frac{1}{2}$	464·7	0·0272
$\frac{1}{2}$	257·2	0·6138	1	440·6	0·0367
$\frac{3}{4}$	207·0	0·5344	2	376·8	0·0523
1	173·0	0·4788	3	328·8	0·0546
$1\frac{1}{2}$	120·0	0·4250	4	285·3	0·0564
2	82·6	0·4000	5	240·1	0·0601
			6	209·3	0·0600
			22	21·1	0·0616

At the conclusion of Experiment XXV., the combustion tube containing the foil was removed to the absorption apparatus, where it was subjected to the prolonged action of hydrogen at dull red heat (650°). After the metal had become fully "hydrogenised," the tube was cooled and the unabsorbed gas withdrawn. The tube was again transferred back to the circulation apparatus, where the rate for normal electrolytic gas was re-determined (Experiment XXVI.). The metal was now found to be extraordinarily active, so much so that pressure records had to be taken every few minutes; by the end of half an hour no less than 83 per cent. of the original gas had disappeared. The values for "k_1" are, for purposes of comparison with the previous experiments of the series, referred to the hour as the unit of time.

Experiment XXVI.

April 15, 1905.
Normal electrolytic gas over surface previously treated with hydrogen at 650°.
T = 400°. Rate of circulation = 1 in 75 minutes.

t.	P.	k_1.	t.	P.	k_1.
minutes.	millims.		minutes.	millims.	
0	497·2	—	15	185·2	1·716
5	355·2	1·754	20	138·2	1·668
10	254·2	1·749	30	80·2	1·585

The remarkable influence of hydrogen on the activity of the metal is strikingly illustrated by the four pressure curves, for normal electrolytic gas, reproduced in Diagram IV., p. 45. Curve A was obtained with the surface in its "normal" condition, and C after complete "dehydrogenation" with oxygen. Curves B and D show the influence of "hydrogenation" at 400° and 650° respectively.

During the course of the experiments just described, a bright mirror of silver had formed along the whole length of the glass rod round which the ribbon had been wound, and the inner surface of the combustion tube had become completely coated with a thin brown film, suggestive of the decomposition of a volatile compound of silver.

Summarising now the results of the four series of experiments, it is evident (1) that with normal electrolytic gas the rate of combination is proportional to the pressure of the dry gas; (2) that the activity of the surface is always greatly stimulated by previous treatment with hydrogen, but not with oxygen; (3) that an "active" surface absorbs hydrogen both at 400° and at dull red heat; and (4) that the behaviour of the "hydrogenised" metal suggests the formation of a hydride rather than the mere occlusion or condensation of the gas. The theory of the catalytic action of the metal indicated by the facts is that it essentially involves the rapid formation and oxidation of a hydride, or at least of a film of "hydrogenised" silver. Two independent velocities, namely, that of "hydrogenation" (V_1) and that of the oxidation of the "hydrogenised" metal (V_2), therefore come into play during the process, and the relative values of the two will, in any particular case, depend on the condition of the surface as regards its power of combining with hydrogen. In the experiments with the gauze, for example, it is evident that V_1 was faster than V_2, for with mixtures containing excess of hydrogen the catalysing power of the surface was quickly stimulated up to a certain limit of complete "hydrogenation," after which the velocity of steam formation was nearly proportional to the partial pressure of the oxygen (*vide* Experiments V. and X.). In the case of the foil, however, it is evident from the results of Experiment XXIII. that V_1 was slower than V_2, for the velocity of steam formation was nearly proportional to the partial pressure of the hydrogen throughout.

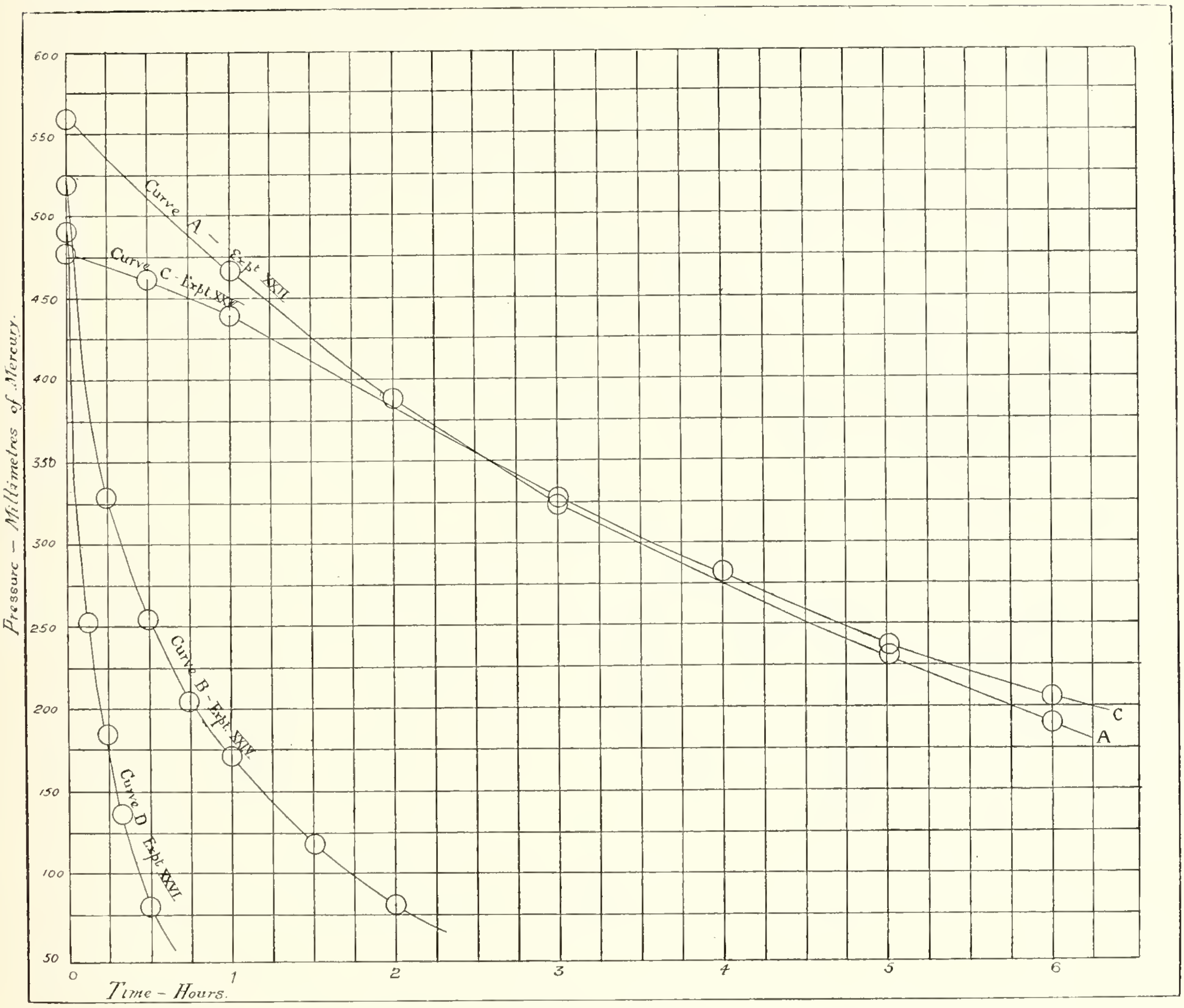

Diagram IV. Experiments with silver foil. Pressure curves for normal electrolytic gas.
Curve A, surface in "normal" condition. Curve C, surface "dehydrogenised" by oxygen.
" B, surface "hydrogenised" at 400°. " D, surface "hydrogenised" at 650°.

Part IV.—Experiments with Gold Gauze.

In order that a series of experiments might be carried out with a gold surface under as nearly as possible the same conditions as the preceding experiments with silver, Messrs. Johnson, Matthey & Co. very kindly prepared a gauze of fine gold wire containing 22 strands (each 0·15 millim. diameter) per centimetre. A rectangular piece of this gauze, measuring 23·3 by 9·25 centims., and weighing 52·9 grammes, was employed for the experiments. The surface exposed to the reacting gases would be approximately 447 sq. centims.

After a preliminary series of experiments with normal electrolytic gas, at different temperatures between 250° and 400°, in which the rate of combination was always found to be proportional to the pressure of the dry gas, we adopted 250° as the best experimental temperature for the investigation of the influence of an excess of each gas, respectively, on the catalytic process. The following three experiments were then made with normal electrolytic gas. In Experiments V. and VI., the gauze was in its "normal" condition, but before Experiment VII., oxygen had been circulated over it at 250° for two days.

EXPERIMENT V. November 25, 1904. Surface in "normal" condition. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.			EXPERIMENT VI. November 27, 1904. Surface in "normal" condition. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.			EXPERIMENT VII. December 1, 1904. Surface after exposure to oxygen at 250° for 2 days. Normal electrolytic gas. T = 250°. Rate of circulation = 1 in 45 minutes.		
t.	P.	k_1.	t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.		hours.	millims.	
0	355·5	—	0	348·6	—	0	339·3	—
1	275·5	0·1107	1	270·9	0·1096	1	257·8	0·1193
2	215·8	0·1084	2	218·6	0·1014	2	204·8	0·1097
3	175·8	0·1019	3	173·6	0·1010	3	166·9	0·1027
4	141·1	0·1003				4	135·9	0·0993
5	112·2	0·1001				5	107·3	0·1000
6	89·3	0·1000				6	84·1	0·1009
7	70·1	0·1007						

It is again evident that the rate of combination is proportional to the pressure of the dry gas, although in all three experiments the amount of change during the first hour was proportionally rather larger than during any of the succeeding hours. From the results of Experiment VII. it is clear that oxygen *per se* has no stimulating influence on the catalysing power of the surface.

In the next two experiments (VIII. and IX.), the influence of an excess of oxygen and hydrogen, respectively, on the rate of combination was studied. The rate of circulation was the same in each experiment (namely, complete circuit in 45 minutes), and during the interval between the two experiments the apparatus stood vacuous.

Experiment VIII.

December 4, 1904.
Original mixture = $H_2 + 2O_2$ nearly. Rate of circulation = 1 in 45 minutes. T = 250°.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	116·6	244·1	—	—
1	85·0	228·4	0·1374	0·0289
2	65·0	218·3	0·1269	0·0242
3	52·3	212·0	0·1161	0·0204
4	43·6	207·6	0·1068	0·0176
5	37·8	204·7	0·0979	0·0153
6	30·8	201·4	0·0964	0·0139
8	19·9	195·7	0·0960	0·0120
10	14·4	192·9	0·0908	0·0102

Experiment IX.

December 8, 1904.
Original mixture = $3H_2 + O_2$ nearly. Rate of circulation = 1 in 45 minutes. T = 250°.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims	millims.		
0	295·7	95·0	—	—
1	251·1	72·8	0·0709	0·1156
2	210·9	52·6	0·0734	0·1283
3	177·8	36·0	0·0736	0·1404
4	150·3	22·4	0·0735	0·1569
5	127·1	10·7	0·0733	0·1897
6	113·7	3·9	0·0692	0·2311

These experiments prove that the rate of combination is mainly determined by the partial pressure of the hydrogen. Throughout Experiment IX., with excess of hydrogen, the values of "k_{H_2}" are remarkably constant, but in VIII., with excess of oxygen, they gradually diminish as the combination proceeds. These conclusions were afterwards confirmed by the results of Experiments XI. and XIV. It would appear that a steadily increasing excess of oxygen has a slight retarding influence.

The stimulating influence of hydrogen, so well marked in IX., was further proved by circulating hydrogen over the gauze at 250° for 4 days, and afterwards re-determining the rate of combination for normal electrolytic gas, as follows :—

Experiment X.

December 12, 1904.
Normal electrolytic gas after exposure of the surface to hydrogen at 250° for 4 days. T = 250°.

t	0	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	4 hours.
P	324·6	257·3	212·8	182·0	157·3	138·9	125·9	103·1 millims.
k_1	—	0·2018	0·1834	0·1674	0·1573	0·1474	0·1371	0·1245.

In this experiment no less than 34·5 per cent. of the original gas disappeared within the first hour, as compared with 22·5 per cent. in Experiments V. and VI. The stimulus was, however, very transient and was hardly noticeable after the first hour.

The foregoing conclusions were confirmed by the following group of four experiments, made under precisely the same conditions as regards temperature and rate of circulation as those just described.

In Experiment XI., an original mixture corresponding very nearly to $3H_2+O_2$ was employed. The rate of combination was again proportional to the partial pressure of the hydrogen; the values "k_{H_2}," it will be observed, are almost identical with those obtained in the corresponding Experiment IX.

In Experiment XII., the rate for "normal" electrolytic gas was determined after hydrogen had been continuously circulated over the gauze at 250° for 5 days, and had then been withdrawn as rapidly as possible from the apparatus.

Experiment XIII. shows the rate for "normal" gas after the gauze had been completely "dehydrogenised" by circulating oxygen over it at 250° for 16 hours. The great difference between the rates observed in these two experiments is a further striking proof of the stimulating influence of hydrogen. Finally, in Experiment XIV., a mixture H_2+2O_2 was employed after the gauze had been completely "dehydrogenised" by circulating oxygen over it for 36 hours at 250°.

EXPERIMENT XI. December 14, 1904. Original mixture = $3H_2+O_2$ nearly. T = 250°. Rate of circulation = 1 in 45 minutes.					EXPERIMENT XII. December 19, 1904. Normal electrolytic gas over "hydrogenised" gauze. T = 250°. Rate of circulation = 1 in 45 minutes.		
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k_1.
hours.	millims.	millims.			hours.	millims.	
0	305·7	100·6	—	—	0	406·9	—
1	258·4	77·0	0·0730	0·1160	$\frac{1}{4}$	325·1	0·3900
2	218·3	56·9	0·0731	0·1237	$\frac{1}{2}$	275·5	0·3388
3	184·9	40·2	0·0728	0·1328	$1\frac{1}{2}$	161·0	0·2685
4	155·5	25·5	0·0734	0·1490	2	137·4	0·2357
5	134·3	14·9	0·0710	0·1659	$2\frac{1}{2}$	119·8	0·2124
6	115·9	5·7	0·0702	0·2078	3	101·8	0·2006

EXPERIMENT XIII.

December 20, 1904.
Normal electrolytic gas over "dehydrogenised" surface. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P.	k_1.
hours.	millims.	
0	399·2	—
$\frac{1}{2}$	355·3	0·1013
1	317·0	0·1002
2	255·9	0·0966
3	200·1	0·1000
4	161·3	0·0984
5	127·4	0·0992

EXPERIMENT XIV.

December 22, 1904.
Original mixture = $H_2 + 2O_2$ nearly. T = 250°. Rate of circulation = 1 in 45 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	109·3	218·7	—	—
1	96·3	212·2	0·0550	0·0132
2	88·1	208·1	0·0468	0·0108
3	81·6	204·8	0·0423	0·0095
5	70·2	199·2	0·0385	0·0081
7	60·0	194·0	0·0372	0·0074
9	50·7	189·4	0·0370	0·0069
11	43·5	185·8	0·0364	0·0064

The Absorption of Hydrogen by the Gold Gauze at 600°.

The results of the foregoing experiments led us to try the action of hydrogen upon the gauze at 600° in the absorption apparatus.* The fall in pressure in each of two experiments amounted to from 30 to 40 millims. out of 760 millims. during the first hour, and in the third experiment the total fall in pressure was 105 millims. during 20 hours. The occluded gas was retained in a vacuum at the ordinary temperature, but could be readily extracted at dull red heat. A microscopic examination of the gauze revealed no signs of disintegration, or of the formation of a hydride, as in the corresponding experiment with silver. The immediate cause of the catalytic action would, therefore, seem to be a merely superficial occlusion, or condensation, of hydrogen, rather than the formation of a hydride or any deep action of the gas. The following re-determination of the rate of combination for normal electrolytic gas at 250°, after the treatment with hydrogen at 600°, showed how greatly the catalysing power of the surface had been stimulated.

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* In speaking of his experiments on the action of hydrogen upon gold at red heat, GRAHAM remarks: "The power of this metal to occlude hydrogen is very sensible." In one experiment it occluded 0·48 of its own volume of the gas ('Phil. Trans.,' 1866, vol. 156, p. 433; 'Chemical and Physical Researches,' p. 275).

Experiment XV.

January 12, 1905.
Normal electrolytic gas over "hydrogenised" gold. T = 250°.
Rate of circulation = 1 in 45 minutes.

t	0	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{2}$	2 hours
P . . .	364·7	189·7	138·3	108·1	62·6	36·4 millims.
k_1 . . .	—	0·5676	0·5612	0·5281	0·5101	0·5004

The influence of hydrogen on the catalysing power of the surface is illustrated in the three pressure curves shown in Diagram V., below. Curve A is for the gauze in its "normal" condition, B shows the transient stimulus imparted by previous exposure to hydrogen at 250°, whilst C shows the more permanent effect of "hydrogenation" at 600°.

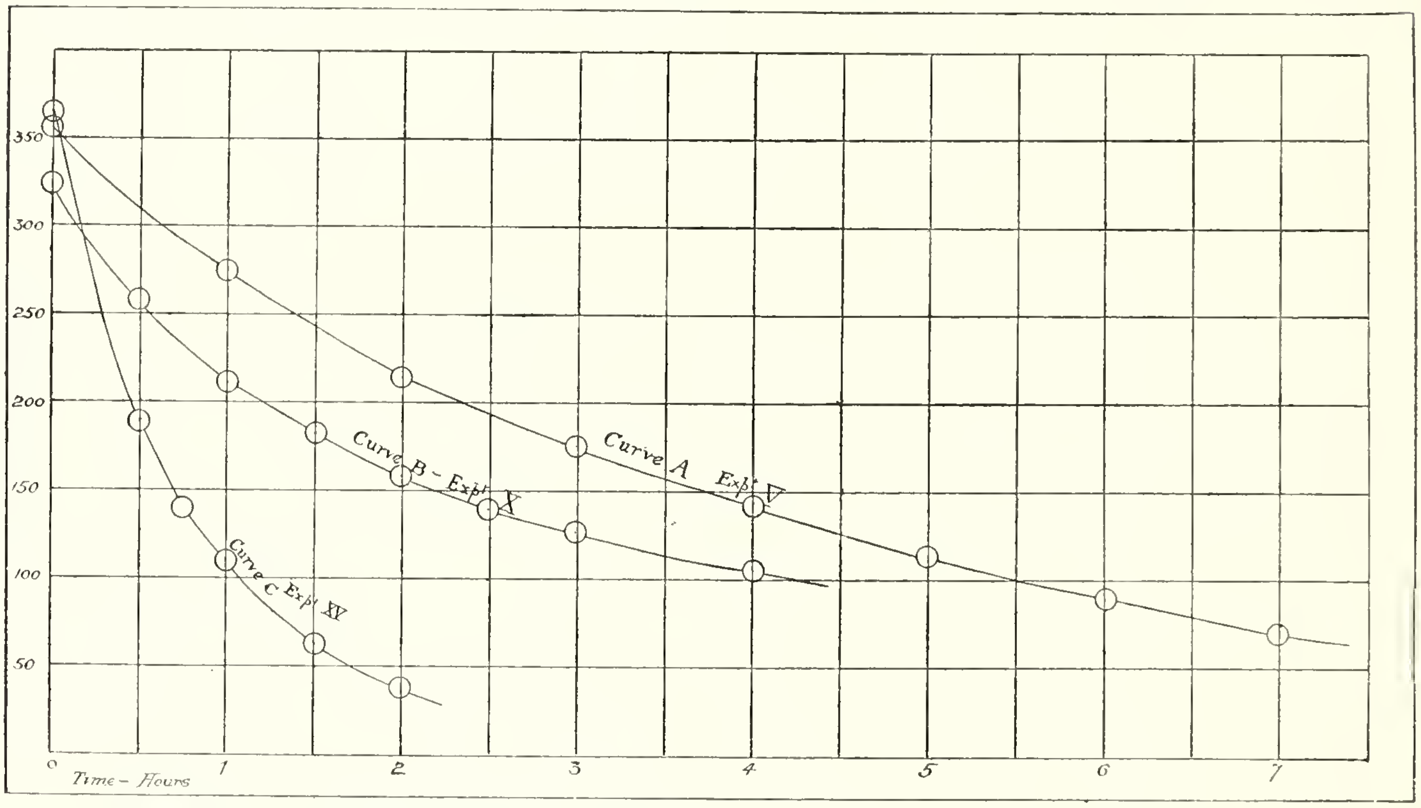

Diagram V. Experiments with gold gauze. Pressure curves for normal electrolytic gas. Curve A, surface in "normal" condition. Curve B, surface "hydrogenised" at 250°. Curve C, surface "hydrogenised" at 600°.

Part V.—Experiments with Platinum.

Bodenstein (*loc. cit.*), from his experiments on the combination of hydrogen and oxygen over a *dry* platinum surface at ordinary temperatures, concluded that whereas an excess of hydrogen has no marked influence on the velocity of the reaction, excess of oxygen produces a considerable acceleration. We cannot entirely endorse this conclusion, at least so far as higher temperatures are concerned, since the following experiments, which were carried out at 160°–170°, show that the action of platinum is not materially different from that of the other metals examined. In the following experiments a piece of platinum gauze (18 strands, each 0·12 millim. in diameter, per centimetre), 7·5 centims. long and 2·7 centims. broad, weighing 2·67 grammes, was employed. The area exposed to the reacting gases would, therefore, be approximately 27·5 sq. centims. The rate of circulation was the same in all experiments, namely, 1 in 65 minutes, but the temperature varied somewhat in different experiments between the above limits.

Experiment I., which gives the "normal" value of "k_1" for the series, proves that with normal electrolytic gas the rate of combination is proportional to the pressure. In Experiment II., where the original mixture corresponded very nearly to H_2+2O_2, the rate was throughout proportional to the partial pressure of the hydrogen, although the values of "k_{H_2}" indicate that the gauze was more than normally active. Experiment III. gives the rate for normal electrolytic gas after the residual oxygen from II. had been circulated over the gauze for 16 hours; there was no evidence of any stimulation. Experiment IV. merely confirms the results of II.

In Experiment V. the value of "k_1" for normal electrolytic gas was re-determined, and in VI. an original mixture corresponding to $3H_2+O_2$ was employed. The rate of combination was again nearly proportional to the partial pressure of the hydrogen throughout. The residual hydrogen was afterwards circulated over the gauze at 165° for 16 hours and finally quickly withdrawn from the apparatus. On re-determining the rate for normal electrolytic gas over the "hydrogenised" surface (Experiment VII.) it was found to be abnormally active. The stimulus, however, rapidly wore away as the experiment proceeded, entirely disappearing after 30 minutes.

EXPERIMENT I. November 26, 1904. Normal electrolytic gas. T = 165–8°. Rate of circulation = 1 in 65 minutes.			EXPERIMENT II. November 27, 1904. Original mixture = H_2+2O_2 nearly. T = 169–173°. Rate of circulation = 1 in 65 minutes.					EXPERIMENT III. November 28, 1904. Normal electrolytic gas after oxygen. T = 170–2°. Rate of circulation = 1 in 65 minutes.		
t.	P.	k_1.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k_1.
hours.	millims.		hours.	millims.	millims.			hours.	millims.	
0	308·8	—	0	123·7	248·5	—	—	0	368·9	—
1	236·6	0·1157	1	68·9	221·1	0·2541	0·0508	½	326·3	0·1066
2	191·5	0·1038	1½	50·1	211·7	0·2617	0·0464	1	286·9	0·1091
3	155·4	0·0994	2½	25·9	199·6	0·2716	0·0381	1½	252·3	0·1101
4	124·5	0·0987	3	18·9	196·2	0·2719	0·0342	2	214·8	0·1174
5	99·9	0·0980	3½	13·9	193·7	0·2712	0·0310	2½	183·5	0·1212
6	77·6	0·0999	4	10·3	191·8	0·2699	0·0281	3	162·6	0·1186
7	56·6	0·1052	4½	7·3	190·3	0·2730	0·0259			
8	40·7	0·1100								

Experiment IV.

December 5, 1904.
Original mixture = $H_2 + 2O_2$ nearly. T = 169–171°. Rate of circulation = 1 in 65 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	115·8	229·1	—	—
1	83·8	213·1	0·1405	0·0314
2	53·0	197·7	0·1697	0·0319
3	36·8	189·6	0·1659	0·0274
4	25·8	184·1	0·1630	0·0237
5	19·8	181·1	0·1538	0·0204
6	14·6	178·5	0·1502	0·0180

Experiment V.

December 14, 1904.
Normal electrolytic gas. T = 161–2°. Rate of circulation = 1 in 65 minutes.

t.	P.	k_1.
hours.	millims.	
0	400·2	—
1	317·2	0·1010
2	250·4	0·1019
3	182·0	0·1141
4	137·2	0·1163
5	101·2	0·1194
6	73·1	0·1231

Experiment VI.

December 20, 1904.
Original mixture = $3H_2 + O_2$. T = 164–5°. Rate of circulation = 1 in 65 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	241·6	80·5	—	—
1	208·0	63·8	0·0650	0·1010
2	182·0	50·8	0·0615	0·1000
3	160·0	39·6	0·0597	0·1027
4	140·4	30·0	0·0590	0·1072
5	123·8	21·7	0·0581	0·1138
6	110·0	14·7	0·0570	0·1229
7	97·2	8·3	0·0565	0·1409
8	86·1	2·6	0·0560	0·1863

Experiment VII.

December 21, 1904.
Normal electrolytic gas over "hydrogenised" gauze. T = 164–5°.
Rate of circulation = 1 in 65 minutes.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	1	2	3 hours.
P	275·6	234·0	214·9	189·4	151·5	129·0 millims.
k_1	—	0·2840	0·2160	0·1628	0·1299	0·1100

PART VI.—EXPERIMENTS WITH NICKEL.

The nickel was employed in the form of a rectangular piece of gauze, containing 10 strands per centimetre, and measuring 15 by 14 centims. The surface exposed to the reacting gases was approximately 330 sq. centims. The metal proved to be a very efficient catalyser, although its catalysing power was rather sensitive to comparatively small changes in temperature. Thus in three preliminary experiments (Nos. I. to III. inclusive) at 200°, 220°, and 240°, the rate of circulation being 1 in 40 minutes, the mean values of "k_1" obtained were 0·010, 0·045, and 0·350 respectively.

The ratio H_2/O_2 for the residual gas from Experiment II. was found to be exactly 2·0, and in the case of Experiment III. it was 2·2. Apparently, therefore, the prolonged action of the gases at 240° caused a slight oxidation of the metal, which, however, did not occur at 220°, the temperature chosen for all the succeeding experiments.

At 220°.

On circulating successive charges of normal electrolytic gas over the gauze at 220°, its catalysing power increased up to a point such that from 12 to 15 per cent. of the gas always disappeared during the first hour of a given experiment. After this point had been reached, however, the values of "k_1" increased regularly during each experiment, as though the activity of the surface was being continually stimulated as the combination proceeded. This induced activity almost entirely disappeared during the interval between two successive experiments, when the apparatus was continuously exhausted. This is shown by the two following experiments with normal electrolytic gas. The rate of circulation for these, as well as all the other experiments of the series, was 1 in from 35 to 40 minutes.

EXPERIMENT IV. May 29, 1905. Normal electrolytic gas.			EXPERIMENT V. May 31, 1905. Normal electrolytic gas.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	514·7	—	0	505·6	—
1	452·1	0·0564	1	437·6	0·0625
2	376·3	0·0680	2	352·9	0·0781
3	301·6	0·0774	3	260·1	0·0962
4	242·9	0·0817	4	199·1	0·1012
5	178·4	0·0922			
7	87·6	0·1099			

The continuous stimulation of the surface in each of the above experiments was not due to any permanent oxidation of the gauze, since the ratio H_2/O_2 for the residual gas at the end of Experiment V. was exactly 2·0. Nor could it be ascribed to a mere reduction in pressure, as the following experiment (VI.) proves.

Before this experiment the apparatus had been continuously exhausted for three days, the combustion tube being maintained at 220° all the time, so as to extract as far as possible any gas condensed or occluded by the metal. A charge of normal electrolytic gas was then admitted, and the rate of combination during the next hour determined. At the end of the hour more gas was admitted until the original pressure was restored, and the rate again determined during the next hour. This procedure was repeated several times. The results showed that whereas the three days' continuous exhaustion at 220° had greatly diminished the catalysing power of the surface, it was subsequently very rapidly restored as the combination of the gases proceeded. The conditions under which this experiment was performed leave no room for doubt but that this rapid stimulation of the surface was due to the progressive condensation of one or other of the reacting gases.

EXPERIMENT VI.

June 18, 1905.
Normal electrolytic gas.

Interval.	Pressure fall.	k_1.
hours.	millims.	
0 to 1	From 510·1 to 497·1	0·0122
1 ,, 2	,, 510·1 ,, 475·1	0·0309
2 ,, 3	,, 509·3 ,, 443·0	0·0614
3 ,, 4	,, 510·0 ,, 421·0	0·0832

The two following experiments (Nos. VII. and VIII.) were made with an original mixture corresponding very nearly to $3H_2+O_2$. In each case, the activity of the surface was greatly stimulated by the increasing excess of hydrogen as the experiment proceeded.

EXPERIMENT VII. June 9, 1905. $3H_2+O_2$.					EXPERIMENT VIII. June 15, 1905. $3H_2+O_2$.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	373·7	124·6	—	—	0	383·0	127·6	—	—
1	322·4	98·9	0·0640	0·1003	1	292·8	83·5	0·1137	0·1842
2	259·4	67·4	0·0758	0·1334	2	203·9	38·1	0·1367	0·2620
3	180·2	27·8	0·1055	0·2172	$2\frac{1}{2}$	169·1	20·7	0·1420	0·3156
4	135·6	5·6	0·1100	0·3391	3	144·4	8·4	0·1412	0·3904

At the conclusion of VIII., the residual gas was as rapidly as possible pumped out of the apparatus, and the rate for normal electrolytic gas immediately afterwards determined (Experiment IX.). The "hydrogenised" surface was now much more than normally active, and the values for "k_1" remained nearly constant throughout. This shows that after a certain degree of "hydrogenation" of the surface, the rate of combination is practically proportional to the pressure of the dry gas.

Experiment IX.*

June 15, 1905.
Normal electrolytic gas over "hydrogenised" surface.

t	0	1	2	3	4	5 hours.
P . . .	505·6	363·7	257·6	179·3	122·1	78·2 millims.
k_1 . . .	—	0·1430	0·1464	0·1501	0·1543	0·1621

In the final experiment of the series, a mixture corresponding to H_2+3O_2 was employed. The excess of oxygen, however, almost prevented any combination, the pressure in the apparatus only falling from 504·8 to 503·0 millims. during the first hour ($k_{H_2} = 0·0042$). This result, taken in conjunction with the results of the three preceding experiments, proves that the catalytic process depends in no way upon occluded oxygen, or superficial oxidation of the metal, but rather upon an association of the surface with hydrogen. A microscopic examination of the gauze at the conclusion of the above series of experiments revealed nothing indicative of any chemical action on the metal (*e.g.*, hydride formation). There had been no pitting of the surface, as in the case of silver, nor were the mechanical properties of the metal at all impaired.

Summarising the results obtained with the four metals examined, we find a substantial agreement in respect of four important particulars, namely, (1) that the catalytic action is in each case primarily due to an association of the surface with hydrogen—in the case of silver probably to the formation of an unstable hydride, in the other three cases to an occlusion of the gas; (2) that with normal electrolytic gas the rate of combination is proportional to the pressure of the gas; (3) that whereas the activity of a surface may always be stimulated by previous exposure to hydrogen at moderately high temperatures, oxygen *per se* has no such accelerating influence, but rather, owing to its "dehydrogenising" action, the reverse; (4) that when an excess of either gas is present, the rate of combination is nearly proportional to the partial pressure of the hydrogen (in the case of silver, however, this only holds good up to a point of "maximum hydrogenation" of the surface).

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* It was at the conclusion of this experiment that the apparatus was continuously exhausted at 220° for three days in order to as far as possible "dehydrogenise" the gauze in preparation for Experiment VI. (June 18, 1905). The result of this operation was to greatly reduce the activity of the surface (*vide* Experiment VI.), where $k_1 = 0·0122$ for the first hour.

The evidence in favour of the "occlusion" theory is particularly strong in the case of nickel, where the "normal" condition of activity can be reduced to almost vanishing point by prolonged exhaustion at a comparatively low temperature. Moreover, the subsequent recovery of activity can be demonstrated by circulating successive charges of electrolytic gas over the surface under conditions which entirely preclude any chemical action of either of the reacting gases on the metal.

PART VII.—EXPERIMENTS WITH EASILY REDUCIBLE METALLIC OXIDES.

It remained now to examine the action of easily reducible oxides, and for this purpose calcined spathic iron ore, copper oxide, and nickel oxide were selected. A necessary condition for the complete success of the experiments was the finding, in each case, of some temperature at which the catalytic combination of the gases would proceed with fair velocity without the surface itself undergoing any permanent change. This condition was fulfilled at 200° in the cases of calcined spathic iron ore and copper oxide, and at 160° in the case of nickel oxide.

A. *Experiment with Calcined Spathic Iron Ore.*

The catalysing material was prepared by calcining fragments of spathic iron ore at dull red heat in a current of air. It contained 79·0 per cent. of ferric oxide and 14·5 per cent. of manganous oxide.

1st *Group.*

The very powerful catalysing action of these oxides at 200° may be judged from the following experiment with normal electrolytic gas. Readings were made every 10 minutes during the first hour, but, for purposes of comparison with later experiments, the values of "k_1" are calculated on the basis of an hour as the unit of time.

EXPERIMENT I.

November 28, 1904.
Normal electrolytic gas. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.	*t*.	P.	k_1.
minutes.	millims.		minutes.	millims.	
0	373·5	—	50	219·0	0·2783
10	336·5	0·2724	60	197·5	0·2767
20	302·5	0·2748	80	163·5	0·2691
30	272·5	0·2738	140	86·7	0·2718
40	243·5	0·2787			

The ratio H_2/O_2 in the residual gas was exactly 2·0, a sufficient proof that there had been no permanent oxidation or reduction of the catalysing material. The remarkably constant values of "k_1" show that the rate of combination was proportional to the pressure of the dry gas throughout the experiment.

In two of the three following experiments (II. and IV.), the original mixture corresponded very nearly to H_2+2O_2; in the third experiment, normal electrolytic gas was employed. The rate of circulation (1 in 60 minutes) was the same for all three.

EXPERIMENT II.

November 29, 1904.
Original mixture = H_2+2O_2 nearly. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	124·8	273·1	—	—
$\frac{1}{2}$	88·8	255·0	0·2956	0·0598
1	63·8	242·5	0·2914	0·0517
$1\frac{1}{2}$	44·8	233·1	0·2966	0·0459
2	32·0	226·6	0·2955	0·0405

EXPERIMENT III.

December 4, 1904.
Normal electrolytic gas. T = 200°.
Rate of circulation = 1 in 60 minutes.

t.	P.	k_1.
hours.	millims.	
0	380·4	—
$\frac{1}{2}$	276·3	0·2778
1	200·0	0·2793
$1\frac{1}{2}$	140·0	0·2895
2	96·0	0·2990
3	43·0	0·3156

EXPERIMENT IV.

December 6, 1905.
Original mixture = H_2+2O_2 nearly. T = 200°. Rate of circulation = 1 in 60 minutes.

t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.		
0	126·4	244·1	—	—
$\frac{1}{2}$	90·8	226·3	0·2874	0·0656
1	66·2	214·0	0·2809	0·0572
$1\frac{1}{2}$	49·6	205·7	0·2708	0·0495
2	39·0	200·5	0·2553	0·0427
$2\frac{1}{2}$	30·8	196·4	0·2453	0·0378
3	24·4	193·1	0·2381	0·0339

These results, which were confirmed by those of similar experiments, prove that in any given experiment the rate of combination is mainly determined by the partial pressure of the hydrogen.[*] If the catalytic process really involves a series of rapidly alternating reductions and oxidations of the material composing the surface, it follows from the facts brought to light in the above experiments (1) that the rate of reduction of the surface by hydrogen at 200° must be excessively small compared with its rate of re-oxidation by oxygen, and (2) that the rate of combination with electrolytic gas must be comparable with the rate of reduction of the surface by hydrogen. That these conditions were not fulfilled will be seen from the following group of experiments :—

---

[*] It may also be observed that, in the four experiments under discussion, the rate at which the hydrogen disappeared was practically the same, viz., about 28 to 30 per cent. during the first hour in each case. This clearly proves that excess of oxygen *per se* has no effect, accelerating or otherwise, on the rate of combination.

2nd Group.

Normal electrolytic gas was circulated at 200° over the material (which for some weeks previously had not been in use) until a constant rate of combination was attained. The two following determinations of the rate for normal electrolytic gas were then made :—

EXPERIMENT V. January 31, 1905. Normal electrolytic gas. T = 200°.			EXPERIMENT VI. February 1, 1905. Normal electrolytic gas. T = 200°.		
t.	P.	k_1.	t.	P.	k_1.
hours.	millims.		hours.	millims.	
0	367·3	—	0	380·4	—
1	293·4	0·0976	1	306·2	0·0943
2	215·1	0·1162	2	235·7	0·1040
3	163·5	0·1160	3	170·4	0·1163
4	126·2	0·1160	4	130·9	0·1158
5	96·4	0·1162	5	100·0	0·1160

The fall in pressure during the first hour in each of these experiments corresponded with the disappearance of as nearly as possible 20 per cent. of the original gas.

Pure hydrogen was next circulated over the surface at 200°, but the pressure fell from 301·7 to 288·5 millims., or by 4·4 per cent. only, during the first hour, a rate of reduction which is many times slower than the rate of combination with electrolytic gas at the same temperature. On raising the temperature of the combustion tube to 300°, the reduction of the surface proceeded with fair velocity, the fall in pressure being about 100 millims. per hour. The reduction was continued until 2¼ litres of hydrogen had been used, an amount exceeding the quantity of hydrogen in four full charges of electrolytic gas.

The apparatus was then thoroughly exhausted during 36 hours, and the temperature of the combustion tube lowered to 200° again. A charge of oxygen was thereupon admitted, and the rate of re-oxidation of the reduced surface determined; the fall in pressure observed during the first hour was, however, only 29·7 out of 406·1 millims., or about 7 per cent., and during the next four hours there was a total further fall of

11 millims. only. These results were fully confirmed in the 3rd group of experiments at 200° in which a new surface of the freshly calcined material was used.

3rd Group.

The rate of combination for normal electrolytic gas over the new surface at 200° corresponded to the disappearance of 27·4 per cent. of the original gas during the first hour ($k_1 = 0·140$). The ratio H_2/O_2 for the residual gas at the end of three hours was 2·0 exactly.

On circulating pure hydrogen over the surface at 200° the pressure fell from 449·5 to 420·4 millims., or by 6·5 per cent. only, during the first hour. After the surface had been reduced at 300° by several successive full charges of hydrogen, oxygen was finally circulated over it at 200°. The pressure now fell from 486·9 to 460·5 millims., or by 5·4 per cent. only, during the first hour.

B. *Experiments with Nickel Oxide.*

For these experiments, the combustion tube of the apparatus was packed with porous lumps of grey oxide of nickel containing 99 per cent. of NiO. After some preliminary trials a temperature of 160° was selected as fulfilling the condition that the gases would combine with fair velocity without the surface itself undergoing any permanent reduction or oxidation. In all the five experiments of this series the rate of circulation was 1 in 35 minutes.

Experiment I., with normal electrolytic gas, gives the "normal" value of "k_1" for the series, and also proves that the rate of combination was proportional to the pressure of the dry gas. In Experiment II., an original mixture H_2+2O_2 was employed; from the values "k_{H_2}" it will be seen that the surface was no more than "normally" active, and that the rate of combination was determined by the partial pressure of the hydrogen throughout. Experiment III., which gives the rate for normal electrolytic gas after the residual oxygen from II. had been circulated over the surface at 200° for 48 hours, proves that its catalysing power had remained unaltered.

Proof that the catalytic process had not involved any permanent reduction or oxidation of the surface was afforded by the analysis of samples of the gas shut off at regular intervals during the course of Experiments I. and II. The ratios H_2/O_2 for the samples in I. varied between 2·05 and 2·10 only, whilst for the samples obtained in III. they were all 2·00 exactly. The falls in pressure obtained during the first hour in these two experiments corresponded with the disappearance of 20·4 and 20·7 per cent. respectively of the original gas. Moreover, the values of "k_{H_2}" in Experiment II. show that the excess of oxygen had no accelerating effect on the rate of disappearance of the hydrogen (exactly 20 per cent. of it disappeared during the first hour).

EXPERIMENT I. May 7, 1905. Normal electrolytic gas. T = 160°. Rate of circulation = 1 in 35 minutes.			EXPERIMENT II. May 8, 1905. Original mixture = H_2+2O_2. T = 160°. Rate of circulation = 1 in 35 minutes.					EXPERIMENT III. May 11, 1905. Normal electrolytic gas after O_2. T = 160°. Rate of circulation = 1 in 35 minutes.		
t.	P.	k_1.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P.	k_1.
hours.	millims.		hours.	millims.	millims.			hours.	millims.	
0	468·5	—	0	150·7	301·4	—	—	0	453·1	—
½	415·0	0·1056	1	120·7	268·4	0·0965	0·0222	½	430·6	0·1070
1	373·0	0·0991	2	100·1	276·1	0·0888	0·0190	1	359·3	0·1007
2	289·5	0·1047	3	80·9	266·4	0·0901	0·0179	2	286·3	0·0997
4	196·1	0·0951	4	64·1	257·8	0·0928	0·0170	3	227·9	0·0995
5	155·2	0·0960	5	51·4	251·3	0·0934	0·0158	4	181·7	0·0992

The rate of reduction of the surface by hydrogen at 160° was next determined, and in order to make the experimental conditions as nearly as possible the same as those in I. and III., a mixture of hydrogen and nitrogen corresponding to $2H_2+N_2$ was employed. The results showed, however, that only 8 per cent. of the original hydrogen disappeared during the first hour as compared with over 20 per cent. in the two experiments with electrolytic gas.

EXPERIMENT IV. May 12, 1905. Reduction of surface by $2H_2+N_2$ at 160°.					
t	0	½	1	1½	2 hours.
P.	460·3	444·3	436·3	431·3	427·8 millims.
P_{H_2}	299·3	283·5	275·5	270·5	267·0 ,,
k_{H_2}	—	0·0464	0·0354	0·0286	0·0243

Finally, after the surface had been reduced by circulating several successive full charges of hydrogen over it (the temperature being raised to 300° in order to accelerate the process), the rate of re-oxidation of the reduced material with oxygen at 160° was determined as follows:—

EXPERIMENT V.

May 17, 1905.
Re-oxidation of reduced surface at 160°.

t	0	1	2	3	5 hours.
P_{O_2} . . .	448·2	415·6	396·3	387·5	376·3 millims.
k_{1O_2} . . .	—	0·0300	0·0253	0·0201	0·0146

The catalytic action of nickel oxide, therefore, resembles that of the reducible oxides contained in calcined spathic iron ore. In both cases it has been proved (1) that the gases will combine quite rapidly without producing any permanent change in the catalysing surface; (2) that the rate of combination with normal electrolytic gas is always proportional to the pressure of the dry gas, and far exceeds either the rate of reduction of the catalysing surface by hydrogen, or its rate of re-oxidation by oxygen; and (3) that when the gases are not present in combining proportions, the rate of combination is solely determined by the partial pressure of the hydrogen.

C. *Experiments with Copper Oxide.*

It had been our intention at the outset of the research to study the catalytic action of copper, as well as that of its oxide, on electrolytic gas. All attempts to obtain reliable velocity measurements in the case of the metal were, however, frustrated by the fact that at even the lowest temperature, where there was any marked action on the gases, the formation of steam was always accompanied by an *independent* oxidation of the surface, at least during the initial stages of an experiment. Nevertheless, it will be necessary to refer to one experiment with copper gauze, since the same gauze, thoroughly oxidised, was employed in the two following series of experiments. The experiment with the reduced gauze is, for purposes of comparison, included in the first series.

1*st Series.*

100 grammes of fine copper gauze, made into a long cylindrical roll, were first of all reduced in hydrogen at dull red heat, and subsequently heated for several hours, and finally allowed to cool *in vacuo*, in order to effect the decomposition of any superficial layer of hydride.

Electrolytic gas was afterwards circulated over the reduced gauze at 214°, when rapid combination took place, as the following pressure records indicate:—

EXPERIMENT I.

September 20, 1904.
Normal electrolytic gas over reduced copper gauze. T = 214°. Rate of circulation = 1 in 40 minutes.

t	0	$\frac{1}{4}$	$\frac{1}{2}$	$\frac{3}{4}$	1	$1\frac{1}{4}$	$1\frac{1}{2}$ hours.
P	384·3	291·8	230·0	176·0	148·5	117·7	87·0 millims.
k_1	—	0·4780	0·4460	0·4520	0·4128	0·4180	0·4360

The values "k_1," calculated in each case on the assumption that the whole fall in pressure was due to steam formation, have really no precise significance, since there was a slight permanent oxidation of the metal (20·7 millims. of oxygen disappeared in this way during the experiment), and the ratio H_2/O_2 for the residual 87 millims. of gas was 4·7. The hydrogen which disappeared as steam was, however, 184·4 out of the 256·2 millims. originally present, or about 76 per cent., in $1\frac{1}{2}$ hours. Inasmuch as a number of other experiments showed that the slight oxidation of the surface was independent of, and had but little influence on, the catalytic process proper, the reaction constant for the latter, $k_1 = 0·3683$, deduced from the partial pressures of the hydrogen at the beginning and end of the experiment, may serve as a fair index of the velocity for comparison with the results obtained in subsequent experiments with the oxidised gauze.

At the conclusion of the above experiment, oxygen was circulated over the gauze at 450°, for about 20 hours, until no further absorption of the gas occurred; its surface was now completely covered with a thick layer of cupric oxide. The temperature of the combustion tube was then lowered to 214° again, and the rate of combination for normal electrolytic gas over the "oxidised" surface determined as follows:—

EXPERIMENT II.

September 23, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.
Rate of circulation = 1 in 40 minutes.

t.	P.	k_1.	k_1 after 1st hour.	t.	P.	k_1.	k_1 after 1st hour.
hours.	millims.			hours.	millims.		
0	437·3	—	—	5	222·4	0·0587	0·0634
1	399·3	0·0395	—	6	187·5	0·0612	0·0656
2	345·4	0·0511	0·0627	7	155·6	0·0641	0·0682
3	299·6	0·0547	0·0622	8	125·4	0·0678	0·0718
4	259·6	0·0566	0·0622				

The ratio H_2/O_2 for the 125·4 millims. of residual gas was 2·11, a circumstance indicative of a slight absorption of oxygen rather than of any permanent reduction of the oxide during the experiment. The values "k_1" for the whole duration of the experiment (third column) indicate, at first sight, a steadily accelerated velocity. Reckoning from the end of the first hour, however, the values given in the fourth column are obtained. The two series of values, therefore, indicate an accelerated velocity during the first hour, after which it varied directly with the pressure of the dry gas.

The most striking feature about the experiment is the extremely slow rate of steam formation as compared with that observed in the previous experiment with the reduced gauze; to put the matter briefly, no less than 8 hours were required with the oxidised gauze to effect the same percentage of change as was observed in 1½ hours with the reduced surface in Experiment I.

The two following experiments at 214° were next made with mixtures originally containing excess of oxygen (H_2+2O_2 nearly), which proved the rate of change to be nearly proportional to the partial pressure of the oxygen.

Experiment III. September 26, 1904. "Oxidised" gauze at 214°. Original mixture = H_2+2O_2 nearly. Rate of circulation = 1 in 40 minutes.					Experiment IV. September 27, 1904. "Oxidised" gauze at 214°. Original mixture = H_2+2O_2 nearly. Rate of circulation = 1 in 40 minutes.				
t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.	t.	P_{H_2}.	P_{O_2}.	k_{H_2}.	k_{O_2}.
hours.	millims.	millims.			hours.	millims.	millims.		
0	144·1	273·6	—	—	0	124·5	259·8	—	—
1	133·5	268·3	0·0332	0·0085	1	112·7	253·9	0·0433	0·0101
2	124·2	263·7	0·0323	0·0080	2	100·1	247·6	0·0473	0·0104
3	110·0	256·6	0·0391	0·0093	3	87·0	241·0	0·0519	0·0109
5	80·9	242·1	0·0501	0·0106	5	62·1	228·7	0·0604	0·0110
7	55·7	229·3	0·0589	0·0109	7	39·5	217·5	0·0698	0·0110
9	34·7	219·0	0·0687	0·0107	9	19·9	207·7	0·0885	0·0108
11	18·9	211·1	0·0802	0·0103	11	3·9	199·6	0·1388	0·0104
13	10·3	206·7	0·0881	0·0094					

Finally, in Experiment V., the rate of reduction of the "oxidised" gauze by hydrogen at 214° was measured; this proved to be something like ten times as fast as the rate of steam formation observed when electrolytic gas was circulated over the "oxidised" gauze at the same temperature in Experiment II. So fast indeed was the reduction process that a charge of 700 cub. centims. of hydrogen introduced into the apparatus almost entirely disappeared within an hour, as the following pressure records for two successive charges indicate :—

EXPERIMENT V.

Reduction of "oxidised" gauze by hydrogen at 214°.

1st charge.			2nd charge.		
t.	P.	k_1.*	*t.*	P.	k_1.*
minutes.	millims.		minutes.	millims.	
0	374·3	—	0	334·3	—
10	208·3	1·5288	10	176·3	1·6692
20	108·3	1·6188	20	103·3	1·5600
30	50·3	1·6272	30	53·3	1·5960
40	22·3	1·7472	40	25·3	1·6896
50	8·3	1·9116	45	16·3	1·7592
60	2·3	2·1600			

2nd Series.

In order to confirm the results of the previous experiments as regards the striking difference between the rate of steam formation with electrolytic gas and copper oxide, and the rate of reduction of the oxide by hydrogen, the gauze was thoroughly re-oxidised at 450°, and subsequently comparative experiments with (1) normal electrolytic gas, and (2) a mixture of hydrogen and nitrogen corresponding very nearly to $2H_2+N_2$, were made at 214°, as follows:—

EXPERIMENT VI.

October 18, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.

t.	P.	k_1.
hours.	millims.	
0	364·5	—
1	316·1	0·0619
2	257·0	0·0759
3	195·4	0·0912
4	151·4	0·0964
5	111·6	0·1028

EXPERIMENT VII.

October 19, 1904.
Mixture $2H_2+N_2$ over "oxidised" gauze. T = 214°.

t.	P.	P_{H_2}.	k_{H_2}.†
minutes.	millims.	millims.	
0	395·7	263·8	—
10	313·2	181·3	0·9774
20	248·2	116·3	1·0671
30	207·6	75·7	1·0844
40	183·1	51·2	1·0680
50	166·8	34·9	1·0542
60	162·8	30·9	0·9313
90	141·4	9·5	0·9624

---

* In order to make these values comparable with those given in other experiments, they have been calculated on the basis of an hour as the unit of time.

† Calculated on the basis of an hour as the unit of time.

The remarkable difference between the results of these two experiments is shown by the two curves for the partial pressures of the hydrogen reproduced in Diagram VI. By substituting inert nitrogen for the oxygen of electrolytic gas the rate of disappearance of hydrogen was increased something like seven-fold, a fact which at once disproves the theory that the catalytic process involves a rapidly alternating series of reductions and re-oxidations of the surface.

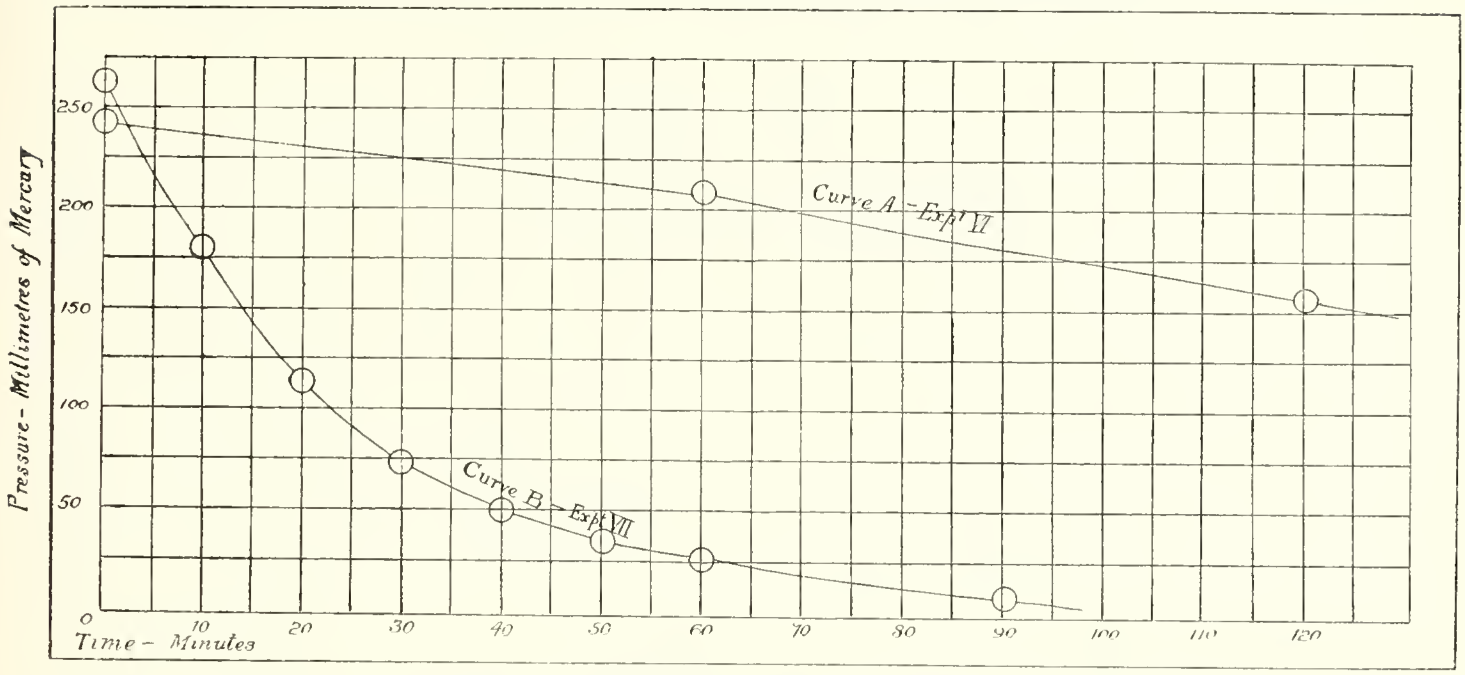

Diagram VI. Experiments with copper oxide. Partial pressures of hydrogen. Curve A, for $2H_2 + O_2$; Curve B, for $2H_2 + N_2$.

In a final experiment (VIII.) the quantity of "oxidised" gauze employed was only 27·8 grammes, instead of the 100 grammes used in previous experiments, in order to extend the combination over a longer period of time. The ratio H_2/O_2 found for samples of the gas shut off in the "bye-pass" tubes during the experiment indicated hardly any perceptible permanent change in the catalysing surface during the first 24 hours, although towards the end of the experiment, when the pressure in the apparatus had fallen considerably, some slight permanent reduction apparently did take place. The rate of circulation was 1 in 40 minutes.

Experiment VIII.

November 4, 1904.
Normal electrolytic gas over "oxidised" gauze. T = 214°.

t.	P.	k_1.	Ratio, H_2/O_2.	*t*.	P.	k_1.	Ratio, H_2/O_2.
hours.	millims.			hours.	millims.		
0	319·9	—	—	12	240·0	0·0104	—
1	312·1	0·0107	—	24	170·0	0·0114	1·96
3	299·0	0·0100	2·0	48	76·1	0·0130	—
6	277·4	0·0103	—	70	29·2	0·0148	1·72
9	258·2	0·0103	1·97				

The fall in pressure during the first hour in the above experiment corresponded to the disappearance of only 5·2 out of the original 213·3 millims. of hydrogen, or less than 2·5 per cent. On subsequently circulating pure hydrogen over the gauze at the same temperature (214°), the pressure fell from 331 to 100 millims. in an hour, representing the disappearance of no less than 70 per cent. of the gas.

3rd Series.

A final series of experiments was made in which the combustion tube was packed with granular copper oxide such as is used in the analysis of organic compounds. The material had previously been heated to dull redness in a current of air for 6 hours, and afterwards in a stream of oxygen for 12 hours longer. The following two experiments were then made at 200°: (1) with normal electrolytic gas (IX.), and (2) with a mixture of hydrogen and nitrogen corresponding very nearly to $2H_2+N_2$ (X.). The rate of circulation was 1 in 45 minutes in each case. It will be observed that whereas only 9·7 per cent. of the original hydrogen disappeared during the first hour in Experiment IX., no less than 50 per cent. of the gas disappeared when nitrogen was substituted for the oxygen of the electrolytic gas.

EXPERIMENT IX. Original mixture = $2H_2+O_2$. Rate of circulation = 1 in 45 minutes.				EXPERIMENT X. Original mixture = $2H_2+N_2$. Rate of circulation = 1 in 45 minutes.			
	t.	P.	k_1.	*t.*	P.	P_{H_2}.	k_{H_2}.
	hours.	millims.		hours.	millims.	millims.	
No permanent reduction of the copper oxide. H_2/O_2 = 2·0.	0	488·8	—	0	333·5	210·7	—
	1	441·7	0·0440	1	226·0	103·2	0·3100
	2	399·1	0·0440	2	162·3	38·5	0·3690
	3	360·0	0·0443	3	131·9	8·1	0·4720
H_2/O_2 = 1·82.	4	319·0	0·0465				
	5	284·5	0·0470				
	6	242·0	0·0509				
H_2/O_2 = 1·47.	8	169·5	0·0575				
	10	120·3	0·0608				
	11	97·8	0·0635				

It is a significant fact that during the first three hours in Experiment IX., when the pressure in the apparatus was fairly high, there was no permanent reduction of the surface; at the end of the sixth hour the ratio H_2/O_2 for the gases was 1·823, indicating incipient reduction, and for the residual gas at the end of the experiment the ratio was 1·469. In this connection it may be pointed out that, so long as there was no appreciable permanent reduction of the surface (say up to about the end of the fourth or fifth hour), the values "k_1" remained nearly constant, whereas at lower pressures, when reduction did set in, they rapidly increased. The same remark applies also to Experiment VIII. with the "oxidised" gauze.

Considering the results obtained with the three different reducible oxides as a whole, they seem to be quite incompatible with any purely chemical explanation of the catalytic process. In the case of copper oxide, it would appear to involve the condensation of a film of "active" oxygen on the surface, and that this film actually protects the catalysing oxide from the attacks of the hydrogen, which would otherwise energetically reduce it. At low pressures the film becomes too attenuated to ensure complete protection, and, in consequence, the formation of steam is accelerated by reason of hydrogen penetrating through on to the oxide and reducing it. In conformity with this idea, the rate of steam formation when the gases are not present in combining ratios was found to be proportional to the partial pressure of the oxygen.

In the cases of the other reducible oxides examined, the fact that the gases combined at moderate temperatures, without permanently altering the surface, and at rates always far in excess of the rates at which either the surface was reduced by hydrogen, or the reduced surface re-oxidised, does not harmonise with the purely chemical theory. It is difficult to resist the conclusion that in these cases also the catalytic action is primarily due to a physical condensation of one or other of the reacting gases at the surface. And since in all experiments where the gases were not present in combining ratios the rate of combination was always proportional to the partial pressure of the hydrogen, it would appear to be the hydrogen which is condensed and so rendered active.

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PHILOSOPHICAL TRANSACTIONS
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SERIES A, VOL. 206, pp. 69–100.

ON THE PERIODICITIES OF SUNSPOTS

BY

ARTHUR SCHUSTER, F.R.S.

NATURAL HISTORY

LONDON:
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II. *On the Periodicities of Sunspots.*[*]

By Arthur Schuster, *F.R.S.*

Received January 7,—Read February 8, 1906.

1. The material used in this investigation consists of:—

(*a*) The series of sunspot numbers collected by Dr. A. Wolf and Dr. A. Wolfer, and published by the latter in his "Astronomische Mitteilungen."[†] This series contains for each month of the years 1749 to 1901 the sunspot frequency as expressed in Wolf's "Relativzahlen."

(*b*) The mean daily areas during each synodic revolution of the sun from January, 1832, to the end of 1900, which have been collected and are issued as a separate publication by the Solar Physics Committee. The publications of the Greenwich Observatory allow us to continue this series to the end of 1902.

(*c*) The Greenwich observations extending from 1883 to 1902, and giving for each day of the year complete statistics of the position and areas of spots. I have used the numbers representing the sums of the daily areas of the whole spots (including umbra and penumbra), the areas being corrected for fore shortening. The unit of area throughout this investigation is the millionth of the sun's hemisphere.

The three series will be referred to as (*a*), (*b*) and (*c*) respectively.

2. The series (*a*) being expressed in different units, the results obtained from it cannot be brought into very accurate comparison with the calculations based on the two other series. Identical units were not necessary for my purpose, but nevertheless it was advisable to investigate in how far a constant ratio existed between the sunspot frequency as expressed in Wolf and Wolfer's series and the same frequency as more accurately determined by means of the measured areas. In Wolf's sunspot numbers, each group of spots is weighted by a number which depends on the average number of spots in the groups visible at the time. If f is the total number of separate spots and g the number of groups, Wolf's "Relativzahl" r is

$$r = \kappa\,(f + 10g) = \kappa g\,(10+n),$$

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[*] Preliminary notice published in 'Roy. Soc. Proc.,' A, vol. 77, p. 141.

[†] 'Vierteljahrschrift der Naturforschenden Gesellschaft in Zürich,' vol. 47 (1902).

if n is the average number of spots in a group. The factor κ depends on the instrument through which observations are conducted, and is taken to be unity for a telescope similar to the one used by Wolf.

In Table I.* I give in separate columns for each year the mean daily sunspot area, as published in series (*b*), together with the mean annual value of Wolf's numbers. The last column, giving the ratio between the two estimates of sunspot frequency, shows a discontinuity about the year 1860, the ratios after that date being markedly higher than those before it. The discontinuity seems to coincide with the time at which the areas began to be measured from photographs. I have therefore separately deduced the ratios for the different portions into which the complete series is divided. It is explained in publication (*b*), that Schwabe's drawings were used up to the end of 1853, and from that date to the end of 1860 Carrington's drawings were made use of in the reductions. For the year 1861 the gap between Carrington's series and the Kew series of photographs had to be filled by means of Schwabe's drawings. The Kew series reaches into the early part of 1872, and as all measurements of areas from 1832 to 1872 were made under the direction of De la Rue and Stewart, we may conclude that there is no great amount of personal equation so far as measurement is concerned. The Greenwich series begins in July, 1873, the gap intervening between the Kew and Greenwich observations being filled by measurements of the Wilna photographs supplied by Professsor Backlund.

Table II. shows the manner in which the ratio of Wolf's numbers to the sunspot areas has varied according to the material on which the measurements were based.

TABLE II.

Series.	Number of years.	Mean area divided by Wolf's numbers.
Schwabe, 1832–1853	22	9·71
Schwabe, including 1861	23	10·00
Carrington, 1854–1860	7	10·79
De la Rue, 1862–1871.	10	16·92
Greenwich, 1874–1901	28	13·38
Total, 1832–1901	70	12·50

The last row gives the mean values as found from Table I.

The larger comparative value obtained when the areas are obtained from photographs is clearly shown by the table. It would seem therefore that Wolf's series as a whole is more homogeneous than that obtained from the measurement of areas. A second fact brought out by Table I. is that the ratios in the Greenwich series are markedly higher at times of sunspot maxima. This shows that in Wolf's method of

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[*] Tables I., IV., V., VI., VII. and VIII. will be found at the end of the paper.

counting, the sunspot activity is over-estimated when the activity is small, or under-estimated when it is large. The direct measurement of areas derived from photographic records gives therefore a greater range of variability between the minimum and the maximum. A further systematic difference will be pointed out in § 13. As it was only necessary for my purpose to bring the different series into approximate coincidence, I have used the mean value of the ratios and multiplied WOLF's numbers throughout by 12·5. This factor, at any rate as regards order of magnitude, reduces them to the scale of sunspot areas.

3. The main object of this investigation was to determine the periodogram of sunspot variability. Let a function $\phi(t)$ of the time t take the values ϕ_0, ϕ_1, ϕ_2, &c., at equidistant values of the time t_0, $t_0+\alpha$, $t_0+2\alpha$, &c., and let it be required to calculate the periodogram of $\phi(t)$ by means of the separate equidistant values.

Put

$$A = \sum_{s=0}^{s=(n-1)\alpha} \phi_s \cos \frac{2\pi}{n} s \; ; \quad B = \sum_{s=0}^{s=(n-1)\alpha} \phi_s \sin \frac{2\pi}{n} s \, ,$$

where n and s are integer numbers, and let

$$S = (A^2+B^2)\,\alpha/p.$$

Then by definition* the average value of S in the neighbourhood of a particular period $n\alpha$ gives the value of the periodogram for that period as derived from the time interval $p\alpha$. The different periods obtained by varying $n\alpha$ should be chosen near together, but there is a limit beyond which it would be useless to go. This limit is reached when the values of A and B for two closely adjoining values n_1 and n_2 are no longer independent of each other. The theory of vibration shows that independence begins when there is an ultimate disagreement of phase amounting to about one quarter of a period, so that if T_1 and T_2 are the times of two periods and the total number of periods is N, independence begins when

$$N(T_1-T_2) = \tfrac{1}{4}T\, ,$$

or when $T_1 - T_2$ is equal to $T/4N$, T being the approximate value of T_1 and T_2.

4. The periodogram may be said to put the statistical material in a form in which it may be most readily discussed, but there may always be cases in which the interpretation is difficult. A few words on this point may therefore prove useful. I do not, of course, claim to have first introduced the application of FOURIER's Theorem to the discovery of hidden periodicities. HORNSTEIN among many others made use of the harmonic analysis, and obtained for the elements of magnetic variations the Fourier coefficients for periods in the neighbourhood of 26 days. The process is sufficiently obvious to have been frequently introduced, but it has generally been assumed that each maximum in the amplitude of a harmonic term corresponded to a

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* 'Roy. Soc. Proc.,' A, vol. 77, p. 136 (1905).

true periodicity. The extent to which this fallacious reasoning has been made use of would surprise anyone not familiar with the literature of the subject.

What distinguishes the method which I am endeavouring to introduce from that of others, is the discussion of the natural variability of the Fourier coefficients according to the theory of probability, independently of any periodic cause which may have influenced the phenomenon. I have shown that where the phenomena are detached, and the probability of the occurrence of any one event does not depend on the occurrence of a previous one, there is a definite probability for the value of the amplitudes of the harmonic terms into which the recurrence of the phenomenon can be resolved. In the more complicated and more frequently occurring cases such a definite probability cannot be assigned *à priori*, but must be determined statistically from the phenomenon itself. Yet there is even in these cases a definite law which defines the manner in which the true periodicity gradually separates itself from accidental variations. The periodogram itself therefore furnishes the material for its discussion, but it is necessary that the investigation should be carried out systematically and extend over a large number of periods. If the statistical data spread over a sufficient range of time, it will often be found convenient to divide the total interval, so as to discover whether the periodogram as determined from one half is similar to that as determined by the other half. Other examples are given in the succeeding investigation illustrating the manner in which a comparatively scanty material may be used so as to give the greatest possible information.

I have so frequently insisted on the optical analogy that it may be worth while to point out that in one respect the periodogram furnishes more definite information than the optical instrument can. The spectroscope only determines the average "intensity," but the periodogram is also able to fix the phase of a periodic variation. Thus if the rainfall were analysed, the periodogram would show a maximum corresponding to the annual variation. With this maximum we may associate the angle determining the phase which will give us the date at which the maximum of the annual period takes place.

In fixing the phase of a periodicity, some care is necessary if the trial period is not exactly coincident with the true period, as otherwise an appreciable error may be introduced. It is necessary to discuss this point in some detail.

If in the expression of § 3 we write tan ϕ for B/A, the angle ϕ measures the phase of the periodicity, supposing there is a true period having a time $T = n\alpha$. But if the true period is T′, the angle ϕ does not correctly represent the phase. To determine the error we may use the equations which I gave in the paper published in the Stokes Volume of the 'Cambridge Philosophical Transactions,' but the following short cut gives substantially the correct result. If we try to fix a simple periodic curve of period T, so as to make it most nearly agree with a periodic curve of period T′ during an interval varying from τ to $\tau+n\mathrm{T}$, we must adjust their phases so that the extreme disagreement is as small as possible, and this is done by bringing the curves to coincidence at the midway point as regards time, *i.e.*, in the present case at a time $\tau+\frac{1}{2}n\mathrm{T}$.

We begin always with the same epoch, but provide for the possibility of subdividing the time interval so as to obtain separately the periodogram of different parts. We therefore must not neglect τ, but we may put it equal to an integral multiple of the trial period, or say to $m\mathrm{T}$. If NT is the total time interval considered, we have thus $n+m = \mathrm{N}$, so that the time at which coincidence of phase is required is $\frac{1}{2}(\mathrm{N}+m)\mathrm{T}$. If now $\cos(gt-\epsilon)$ is the true periodicity and $\cos(\kappa t-\phi)$ that of the trial period which is to be adjusted so as to fit the true period most nearly, we must put

$$\tfrac{1}{2}g(\mathrm{N}+m)\mathrm{T}-\epsilon = \tfrac{1}{2}\kappa(\mathrm{N}+m)\mathrm{T}-\phi\,,$$

therefore

$$\epsilon-\phi = \tfrac{1}{2}(g-\kappa)(\mathrm{N}+m)\mathrm{T} = \pi\frac{\mathrm{T}-\mathrm{T}'}{\mathrm{T}'}(\mathrm{N}+m).$$

This determines the difference in phase between that belonging to the true period and that determined with a slightly erroneous trial period. Table III. gives, *e.g.*, the angle ϕ in the neighbourhood of the 11-year period, and shows how the phase of the true periodicity may be determined. This periodicity, it will appear, is only prominent in the second portion of the complete time interval considered. The first column gives the times of the trial periods in years. The second and third columns give the values of N and m; in the fourth column is given the phase as calculated by the trial period, the fifth gives $(\epsilon-\phi)$ the difference of the phases between the trial and true periods calculated by means of the above equation on the supposition that the true period was 11·125 years. The last column gives the calculated phase of the true period. In calculating the last column from the two preceding ones it must be borne in mind that 360° or any multiple thereof may be added or subtracted from an angle representing a phase without alteration of its significant value.

TABLE III.

T.	N.	m.	ϕ.	$\epsilon-\phi$.	ϵ.
9·75	15	7	107°	−129°	−22°
10·00	15	7	35	41	− 6
10·25	14	7	306	297	+ 9
10·50	14	7	221	212	9
10·75	14	7	142	127	15
11·00	14	7	50	− 42	8
11·25	13	6	335	+ 38	13
11·50	13	6	250	115	5
11·75	13	6	180	192	12
12·00	12	6	107	255	2
12·25	12	6	37	328	+ 5
12·50	12	6	317	401	− 2
12·75	11	5	259	+421	−40

The table shows in a remarkable manner how, quite independently of the intensity, the 11-year period ruled the periodogram during the interval considered. The phases ϕ are in regular progression, the intervals between two succeeding ones being almost equal. The last column gives the phase of the true period. As the calculation is only strictly applicable to periods near the real one, we may take 10° as the phase of the period as determined from the table. This gives for the time of the maximum $11\cdot125 \times \frac{10}{360} = 0\cdot31$ years, after the epoch which was 1749·25. The times of the other maxima are therefore included in the expression $1749\cdot56 \pm 11\cdot125n$, or, as we may also put it, $1905\cdot31 \pm 11\cdot125n$, where n is an integer number.

5. In order to obtain the periodogram for periods having a length of several years, it is obviously necessary to use as long a series as possible. I have consequently had recourse to WOLF's and WOLFER's monthly numbers, beginning with the year 1749. I have used the numbers given by WOLFER as "observed," and not those obtained by a process of smoothing, which are given in a separate table under the heading of "compensated numbers." The process of smoothing I consider to be a harmful process, and quite unnecessary when periodicities are to be examined by a scientific process.

Each year was divided into two equal parts, and the sums of the numbers for each half-year were calculated. These sums represented therefore six times the mean sunspot activity for the first and second halves of the year respectively. The values of A and B in the above expressions were then found. For this purpose the six-monthly values were, as is customary, arranged in rows containing as many figures as there are intervals of six months in the selected period. Thus, to get the value for twelve years, each row contained 24 numbers. The number of rows was arranged so as to get in as many complete periods as possible, beginning always with the total sunspot number for the first six months of 1749. We may therefore consider April 1, 1749, to be the epoch which determines the phase of all the periodicities derived from the series (a).

As twelve periods of twelve years bring us to 1894, there was not sufficient material to include a further complete period, and the calculations had to be stopped at that point. The sum of the twelve rows of 24 columns, in the example chosen, having been formed, the expressions for A and B are easily calculated by substituting $p = 288$ (which is twice the total number of years included). The year being the unit, and the intervals between the times to which successive numbers refer being six months, we must put $\alpha = 0\cdot5$. The ordinate of the periodogram will then be $(A^2+B^2)/144$. The factor in the denominator varies slightly for different periods, and sufficient accuracy is obtained by taking the divisor to be 150 in all cases.

As the sum of six successive sunspot numbers was used in place of the average during the corresponding interval, the result must be divided by 36 in order to bring it to WOLF's scale, and multiplied by the square of 12·53* or 157, in order finally to reduce the result to the unit based on the measurement of areas. The method is available for all periodicities containing an integer multiple of the half year. In some cases it was advisable to obtain the periodogram for periods lying halfway between those to which the above method is directly applicable. The successive rows in the original table were then arranged so as alternately to contain a number of figures differing by one. Thus, for a period of $7\frac{3}{4}$ years the alternate rows were formed of 15 and 16 figures. This gives 31 intervals of six months for two complete periods, or on the average $7\frac{3}{4}$ years. In the last column alternate numbers were missing, and this column was omitted in the calculations for A and B, the number n being chosen to correspond to the number of columns retained. In some cases it is more convenient for the tabulation of the angles and of their trigonometrical functions to include the last column, which must in that case be multiplied by a factor correcting for its smaller number of entries. When a certain period has been treated, and the half or the third of that period is to be introduced, it is not of course necessary to form again the system of rows and columns, but we may proceed as in the calculation of the sub-periods of FOURIER's coefficients. The equations are then replaced by

$$\mathrm{A} = \sum_{s=0}^{s=(n-1)a} \phi_s \cos \frac{2m\pi}{n} s; \quad \mathrm{B} = \sum_{s=0}^{s=(n-1)a} \phi_s \sin \frac{2m\pi}{n} s,$$

where m is two or three, according as the half or the third of the original period is required. (See Table IV., p. 97.)

6. The second column of Table IV. contains the ordinates of the periodogram, calculated from the complete record in the manner described, and in fig. 1 the periodograph is drawn. The great intensity of the 11-year period is well shown, but the shape of the curve for periods between 10 and 11 years and some other features seemed to require further elucidation. I therefore divided the whole period of 150 years into two portions, which were nearly equal to each other. This could be done accurately when the original table contained an even number of rows, but when the number was uneven, so that the two portions could not be made exactly equal, the first portion was always taken to be the shorter one. In consequence, the epoch of the beginning of the second portion varies somewhat; the exact dates are given in column 5 of the table, the Roman numeral attached to the year indicating whether it is the first or second six-monthly value which forms the beginning of the group of periods. Where no such Roman numeral is given, the sunspot numbers for the whole year were used in the calculations.

For some purposes it would have been better to have chosen a fixed epoch for the

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[*] The general mean during the years 1832–1901 inclusive as given in § 1 is 12·50. When this investigation was commenced the areas for the year 1901 were not available. The number given in the text above, which is the mean found when 1901 is excluded, was used in the calculations. The difference is of course insignificant.

beginning of the second and more important part of the series, in spite of the greater labour of calculation which this would have involved. But it was necessary to be able to compare the phases of the oscillations which the two halves yield separately. On the whole the balance of advantage seemed to lie with the method adopted.

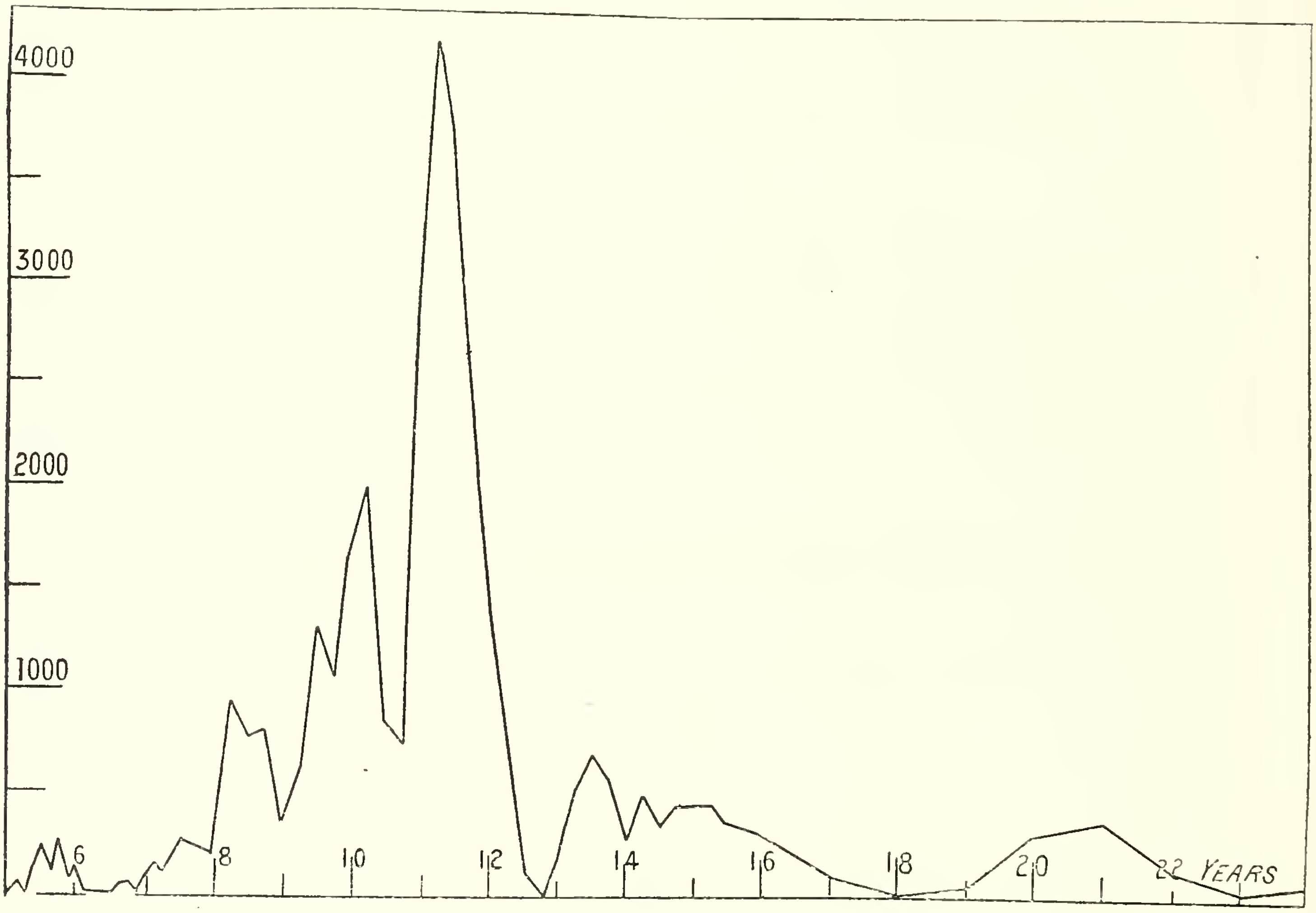

Fig. 1.

Columns 3 and 4 of Table IV. give the numbers obtained for the periodogram when the whole range is divided into two portions, and fig. 2 represents the numbers in a graphical form, the curve A being the periodograph belonging to the last 75 years.

The result is striking. The two curves have no resemblance to each other. Looking at them, we might think that they illustrate two entirely different phenomena. The truth is that between 1750 and 1820 the 11-year period, though existing, had a slight intensity, being quite overpowered by two others with periods of about $13\frac{3}{4}$ and $9\frac{1}{4}$ years. It may be argued that the observations during the eighteenth century were too scanty and uncertain to allow of any such definite conclusion, but I do not believe that the decisive verdict of the periodogram can be disposed of in this way. The main features of the curves are determined by the times at which the maxima occurred, and to a minor extent by the estimate of the activity at these maxima. The uncertainty which probably does exist near the times of the minima does not appreciably affect the result, as the periods of maximum activity as well as the intensities at these periods are sufficiently well known. There is, moreover, the direct evidence of the periodograph curve that the absence of the 11-year period is not likely to be due to accidental causes. Uncertainty in the observations would act in the direction of giving a broad band extending over a wide range of periods, but would not, except through a freak, give the two pronounced maxima which curve B shows.

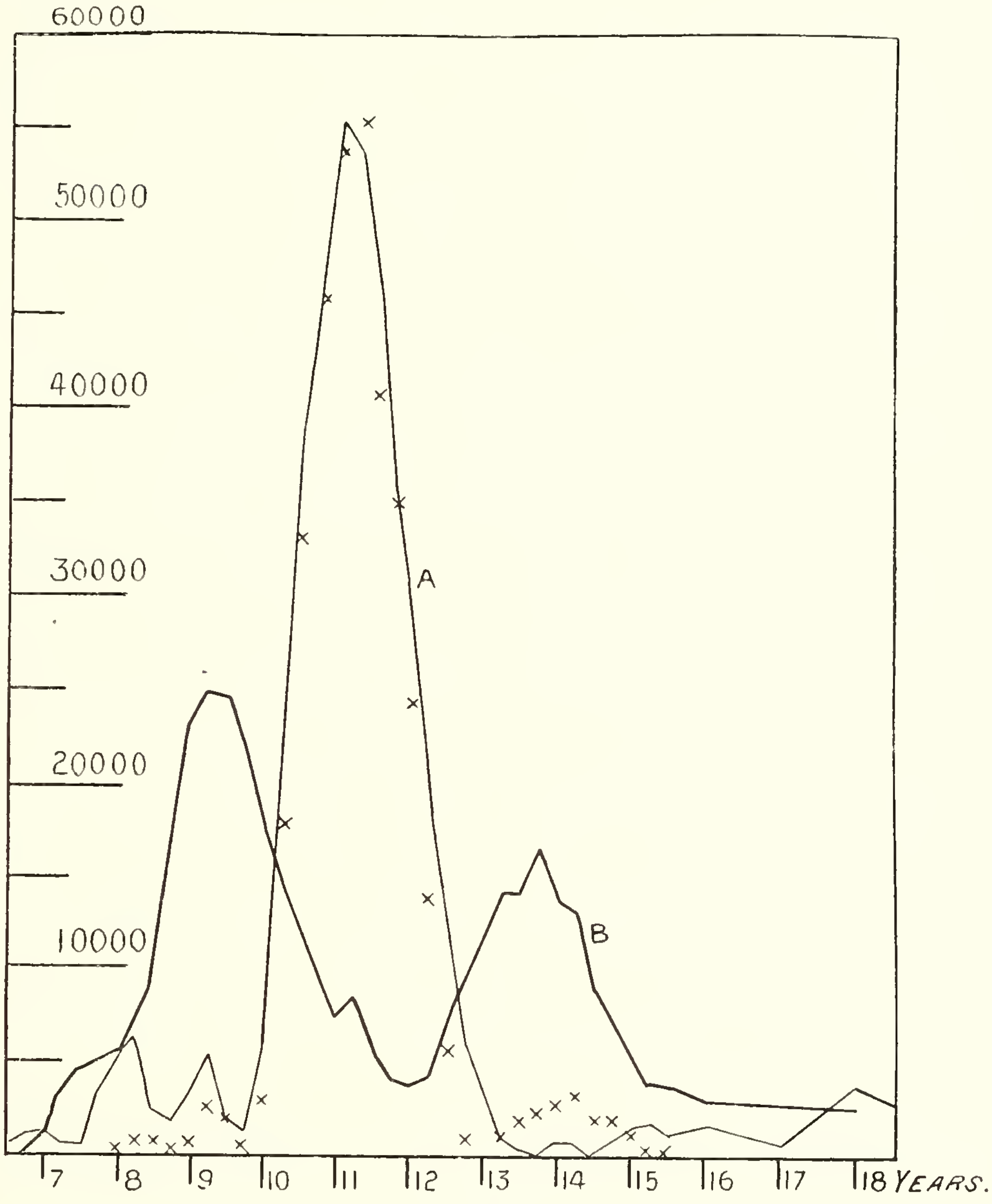

Fig. 2.

A closer inspection of the sunspot curves, as plotted down by WOLFER, shows that the two periods for which curve B shows its principal maxima were active successively rather than simultaneously. It appears that the period of 9 years is the important one as regards the observations previous to the maximum of 1788, while that of 13 and 14 years is brought in through the variations observed between 1788 and 1829. It would seem that more or less irregular variations, showing maxima of intervals of rather more than 9 years, were succeeded about 1788 by three unequal but long periods of 17·1, 11·2, and 13·5 years, respectively, and these afterwards settled down to a fairly regular periodicity of 11·1 years. It will appear that the periodicities in question are probably never quite extinct, but that the chief part in ruling the sunspot phenomena is sometimes taken up by one and sometimes by another period.

During the 75 years to which the curve A applies the shape of the periodogram is very nearly that which a true and, in the optical sense, homogeneous period would give. In order to show this, I have marked in fig. 2 by means of crosses the points through which the periodograph would pass if the period was a simple[*] one of 11·125 years. These crosses will be found to lie close to the actual curve. A curve drawn through the crosses, marking the periodograph of a homogeneous period, would show a small but appreciable rise corresponding to the periods of $9\frac{1}{4}$ and $14\frac{1}{4}$ years, and rather less marked elevations for shorter and longer periods. These secondary elevations correspond to the diffraction bands seen on the two sides of the central maximum of a spectroscopic line. It has already been pointed out in § 4 that the phases of the periodicities of nearly 11 years are in arithmetical progression such as we should expect if the main period were homogeneous.

Reference to Table IV. shows a decided maximum corresponding to a period of 5·625 years in the second half of the complete time interval. This is undoubtedly to a great extent due to the first sub-period of the 11·125-year cycle, though the displacement in time is greater than it should be. This maximum seems to exist to a much smaller degree in the first half of the interval. Further features of the table and curves will be referred to later.

The periodicity corresponding to the time of revolution of Jupiter (11·86 years) has been examined, but reference to Table IV. shows that there is no evidence of a periodicity connected with the orbital revolution of that planet. In fact, we may definitely assert that no influence directly traceable to Jupiter exists.

7. It has been stated that in the absence of definite periods the expectancy of the intensity of the periodogram must be obtained from the periodogram itself in all cases where the events to be analysed are not, as regards their succession, independent of each other. The expectancy not depending on the period, we may select for the purpose any portion of the curve in which we have no reason to suspect any periodicities. The portion most suitable for this purpose in our case is that lying between 54 days and 1·5 years. Shorter periods must be avoided, because if the length is only a few days the intensity of the periodogram is depressed, owing to the fact that sunspots as a rule last several days. That this is so may easily be recognised by imagining all the sunspots to have the same duration, each spot also keeping the same area during the whole course of its life. It is obvious that in this case the period having a length equal to the life of the spots would be totally absent.

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[*] A simple period is one represented by a circular function.

When we come to periods which are near to that of the solar rotation, periodicities appear, owing to the fact that some of the spots persist during more than one rotation. This effect will, however, disappear when the period is well above that of the solar rotation. When the periods come near to 1·5 years, the sub-periods of well-ascertained periodicities make their presence felt. Hence the limits chosen for calculating the natural intensity of the periodogram must be confined to about 35 days on the one hand and 1·5 years on the other. The average intensity of these periods may be determined from Table VI., and is found to be 15,000. The probability of an intensity greater than h times the average value is e^{-h}, and we may perhaps begin to suspect a real periodicity when this value is 1 in 200. This gives 5·3 as the value of h and 80,000 as the smallest value of the intensity which invites further discussion. When h has the value 8, the probability of an intensity greater than h times the expectancy is 1 in 3,000 and we may begin to be more confident that there is some definite cause at work to bring up the periodogram to that value. The intensity in that case is 120,000. When h is 16, the chances of being misled by accident is only one in a million.

8. Periodic times between 5·18 years and about 2 years were investigated by taking as basis the mean sunspot areas for each assumed synodic rotation, as given in publication (*b*). For this purpose four successive numbers, as given in the tables published by the Solar Physics Committee, were added together, and rows were formed containing a number of successive entries. The longest period chosen was that containing seventeen times four, or 68, synodic rotations, each assumed to be of duration 27·275 days, giving a period of 5·18 years. The process was repeated by forming tables containing columns varying in number between 10 and 17, and intermediate periods were treated by the well-known process of shifting successive rows to the right or left. The semi-periods were treated in the usual manner. Table V. gives the result, which is graphically represented in fig. 3, curve A. The periodogram curves, as deduced from Wolf's sunspot number in the manners explained above, are shown in curves B and C, the former referring to the second, and the latter to the first half of the total range of 150 years.

The main features of curve A are formed by the elevations at 2·69, 3·78, 4·38 and 4·78 years. The first two of these elevations are in all probability only due to sub-periods, being the second and third harmonic of the 11·125 variation which we should expect to find at 2·78 and 3·71. The divergence between the observed and calculated periods is probably not more than may be accounted for by superposed irregularities. The rise at 4·38 does not occur on curve C and only to a slight extent on curve B, but the intensity as determined from the areas is sufficient to make the reality of the period probable. There is also a slight rise of doubtful reality at a period corresponding to 4·08.

9. With regard to periods which are shorter than 1·89 years, the labour of a complete investigation which would have to secure that no existing periodicity could escape notice would be very great. I have, therefore, for the present considered only

some of the special periodicities, the existence of which has been suspected, leaving a more detailed investigation for future treatment. In order to find the average values of the periodogram within this region, the mean sunspot areas (publication *b*) were grouped so that the times of the period were 16, 18, 20, ... 30 solar rotations. Each group was divided into four parts, corresponding to a division of the whole material, extending from 1832 to 1900, into approximately equal intervals of time, each such interval being therefore about $16\frac{1}{2}$ years. The mean intensity of the four groups for each period gives us a better estimate of the mean intensity of the periodogram than the values obtained from the group as a whole. If a periodicity were suspected, then of course the combined intensity of the whole time interval would have to be calculated. For the special investigation of a possible periodicity corresponding to the synodic revolution of Mercury, two tables were formed in which each row consisted of the numbers belonging to 4 and 5 rotations respectively, and each such table was subdivided into six groups. The calculations were completed by obtaining in each case the coefficients of the semi-periods. The results are given in Table VI.

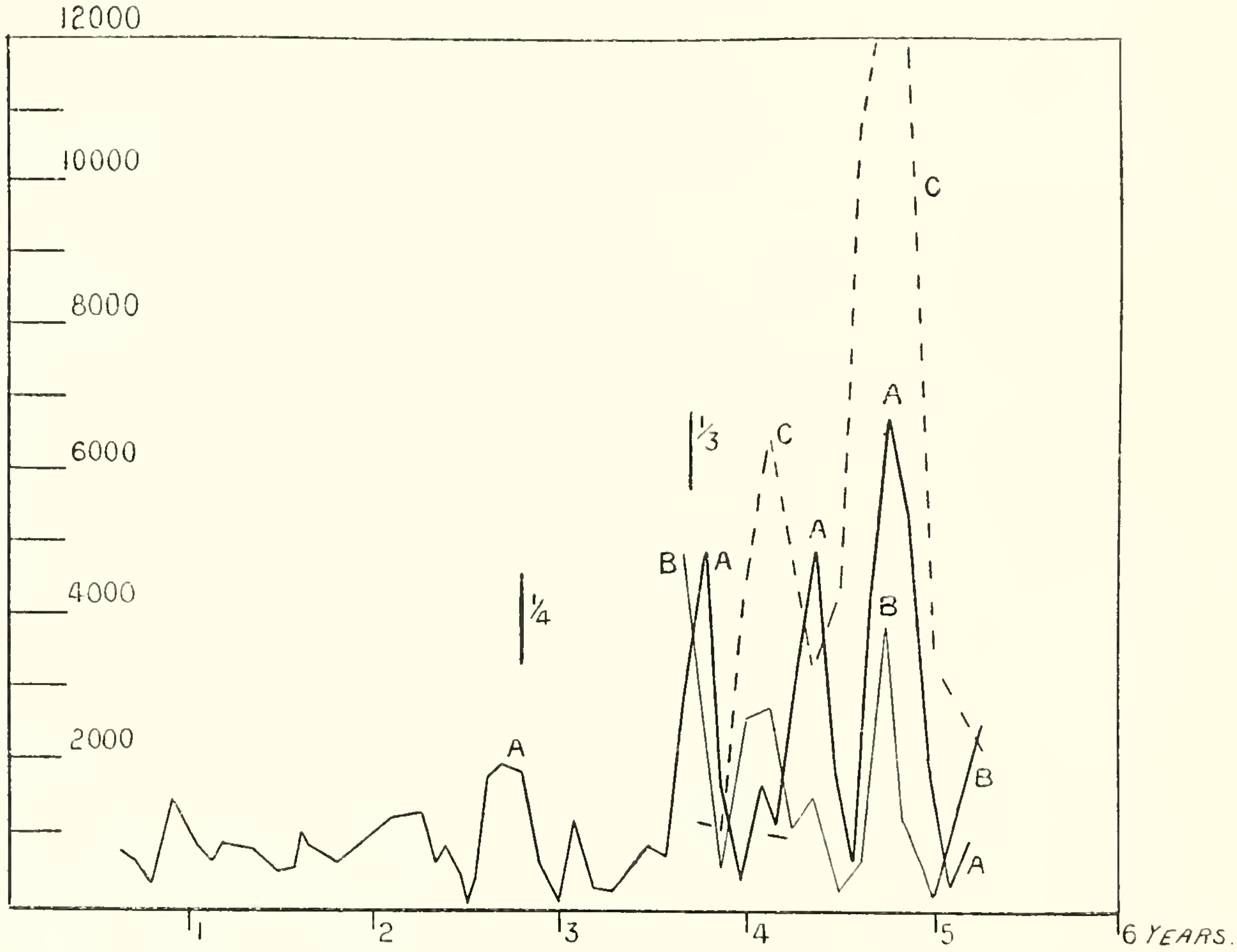

Fig. 3.

For periods of still shorter duration the Greenwich results (*c*) had to be used. The available time interval, extending from 1886 to 1900, was divided into three sets of five years each, and periodic times of 24, 25 . . . . . 30 days were investigated, together with their first sub-periods. The intensities of the periodogram depend to a great extent on the particular part of the 11 years' cycle which is being investigated, the variations being greater when the intensities are great. The data are not sufficient to deal with a considerable number of cycles, and the correct average cannot be formed. I therefore give the values for each of the three groups 1886–90, 1891–95, and 1896–1900, the middle one of which coincides with a period of great activity. The numbers are collected in Table VII. There is a great variability in the numbers, but if a mean value is obtained for each period, and then, as in the last column of the table, an average of three successive periods is formed, a good agreement is obtained.

It will be noticed that somewhere between 15 and 24 days a considerable rise in the intensity of the periodogram takes place. This was to be expected. In the first place there must be a depression in the value of the intensities for short intervals of time due to the length of life of a spot. It has already been pointed out that if all spots lasted exactly the same time, the intensity of the periodogram would be zero for periodic times equal to this duration. The depression in the actual case will spread over a considerable range of periods, and will not allow the full value of the intensity to show itself until times which are at least twice as long as the average life of a spot. Such of the larger spots as come into view at one edge and traverse the whole disc would furnish a contribution to the periodogram in which the periods corresponding to half the synodic revolution are absent, provided the area covered by the spot is constant. We might therefore have expected a specially low value in the intensities corresponding to periods between 13·5 and 14 days. This is not shown by the tables, a fact probably accounted for by the great variability of the area of a large spot as it traverses the disc.

The periodic re-appearance of spots during successive rotations of the sun should increase the intensity for periods approximating to the average rotation period. A definite periodicity must not, however, be expected, quite apart from the fact that the rotation period itself is indefinite. The re-appearance of a phenomenon at regular intervals of time only constitutes an approximately homogeneous periodic phenomenon when the re-appearances are sufficiently numerous. With a life of three or four rotations only, there can be little distinction between periodicities ranging from 25 to 29 days.

The comparatively large value of the periodogram (2400) for a period of 13·25 days deserves some notice. Both in the interval 1890–95 and 1895–1900 there is a very decided rise of intensity corresponding to that period. But if the periodicity were real, the phases should be in regular progression. This is not the case, though we may obtain a better agreement by slightly altering the periodic time to 13·296 days. Treating the whole interval of fifteen years, the intensity is found to be 3080. If there were a real period, the increase should be much larger than this, and for the present we must therefore treat this period as accidental.

The literature connected with the relation between solar terrestrial phenomena is full of supposed periodicities approximately coinciding with that of a solar rotation. Most of these periods are in the neighbourhood of 26 days, a time agreeing neither with the sidereal nor the synodic rotation, but it seemed worth while to investigate whether any definite periodicity in the sunspot areas can be discovered which takes place in a period near to that of 26 or 27 days. I have for this purpose worked out the Fourier coefficients of these two periods separately for each of the 15 years, 1885–1900. The deduced values of the periodogram and the phases are given in Table VIII. By a graphical method, explained in my discussion of the Magnetic Declination,* the periodicities of specially large intensity lying near the two selected times may be determined. Applying this method, I have not been able to discover any variation which suggests a true periodicity. The mean value of the periodogram for the periods of 26 and 27 days, as determined from individual years, agrees well with the general average shown by the last column of Table VII., which was based on a time range of 5 years.

10. A planetary influence on sunspots has often been suspected, and I have therefore specially considered the rotation periods of Jupiter, Mercury, and Venus. Table I. shows, as already pointed out, that the rotation period of Jupiter (11·86 years) gives no increased intensity to the periodogram. As regards the planets Venus and Mercury, Professor TURNER kindly sent me a list of the dates of their upper conjunction with the earth since 1833. Tables were formed in which, in the case of Venus, the values of the sunspot areas during 21 successive rotations were arranged in order, the first column always giving the sunspot area for the rotation during which upper conjunction took place. The synodic revolution of Venus being approximately 21·4 rotations, the tables so arranged could be used to determine the Fourier coefficients for the rotation period. In the case of Mercury the same process was followed, except that there were only four columns corresponding to the four complete solar rotations which take place within one synodic orbital revolution of the planet. Table VI. shows a small rise in the periodogram corresponding to the rotation period of 1·5986 years, which is that of Venus. The number given is the mean value of four, obtained by splitting the 68 available years into four periods of 17 years.

It is found that the phases for the four separate intervals do not agree, so that, if we combine the whole series of years, it is found that the periodogram intensity is smaller than the average. The synodic revolution of Mercury (115·88 days) similarly gives an exceptionally small value for the intensity of the periodogram. The semi-periods also show no effect.

11. We may now turn to the special consideration of the periodicities which have been found. The most persistent of the periods indicated by the periodogram is one having a period of about 4·8 years. It appears separately in the two series of WOLF's numbers and is confirmed by the records based on the measurement of areas.

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* 'Cambridge Phil. Soc. Trans.,' vol. 18, p. 107 (1899).

Appearing without much change in intensity throughout the time that sunspots have been observed, it has been more regular in its activity than the period of 11 years which hitherto has been the only one recognised.

To determine more exactly the periodic time, we may compare the phases as found from the two half intervals of Wolf's series, starting with the assumed period of 4·75 years. We thus find that there has been an acceleration of phase of 96° 43′ in the two portions which are separated by 16 complete periods. This change of phase is corrected by taking the periodic time to be 4·83 years. If we turn to the more accurate data derived from the measurements of areas, we find the maximum to lie at 4·78, but the change in intensity with increasing or diminishing periodic time suggests a somewhat longer period. A rough graphical interpolation seemed to give 4·81 years as the most probable length. Desiring to fix the time as accurately as possible, I arranged the records so as to give the intensity for this period and obtained 131,500, which is decidedly less than when a period of 4·78 years is assumed. This leaves us then with a certain amount of doubt as to the correct period, but the difference in the two values found would in 14 periods accumulate only to the extent of displacing the maximum by six months.

The phase as derived from the measurements of areas gives September 9, 1836, as one of the maxima, assuming the period to be 4·81 years, and September 21, 1836, if the period is 4·78 years. Wolf's numbers with a period of 4·83 years give February, 1836, as the corresponding date of maximum phase. Table IX. contains the dates of the maxima of the periods according to the two suppositions. The civil dates are only approximate and are derived from the fraction of the year. In comparing these dates in the future with the maxima as they occur, it will have to be noted that the phases given are those of the simple period, and that the higher harmonics have the effect of slightly postponing the maxima of the fundamental period.

Table IX.

4·81.	4·78.	4·81.	4·78.
1831·9 (November 17)	1831·9 (December 10)	1875·2 (March 3)	1875·0 (December 17, 1874)
1836·7 (September 9)	1836·7 (September 21)	1880·0 (December 23, 1879)	1879·7 (September 28)
1841·5 (July 1)	1841·5 (July 1)	1884·8 (October 15)	1884·5 (July 10)
1846·3 (April 23)	1846·3 (April 13)	1889·6 (August 7)	1889·3 (April 22)
1851·1 (February 13)	1851·1 (January 2)	1894·4 (May 29)	1894·1 (January 30)
1855·9 (December 5)	1855·8 (November 4)	1899·2 (March 21)	1898·9 (November 11)
1860·7 (September 27)	1860·6 (August 15)	1904·0 (January 11)	1903·6 (August 22)
1865·6 (July 19)	1865·4 (May 27)		
1870·4 (May 11)	1870·2 (March 4)		

The average amplitude of the period has been 98; that of the 11-year period being 586.

Perhaps the severest test we can apply to prove the reality of the period is to consider the individual maxima at times when otherwise the sunspot activity is small. The maxima of December 4, 1855, December 23, 1879, and August 7, 1889, satisfy that condition. According to the records tabulated by the Solar Physics Committee, the sunspot activity between March 15, 1855, and July, 1856, was exceedingly small, rising above 30 (the unit is the millionth of the sun's hemisphere) only in the two rotations beginning October 20 and November 16. During the latter rotation the area was 61. The only notable outbreak during 16 months, therefore, took place at a time closely coincident with the theoretical maximum. According to CARRINGTON's drawings the spots seen were close to the equator and in the northern hemisphere.

At the end of 1879 the sunspot activity began to increase again towards the maximum, which took place five years afterwards. The first notable outbreak took place during the rotation which began on December 30, closely following the maximum of the period we are considering.

The year 1889 was one of minimum activity, though spots were occasionally observed. The sunspot areas in the rotations beginning on July 21 were 345, the four preceding rotations gave 19, 17, 160, 214, and the four following ones 101, 59, 2, 0. There was here, therefore, a very sharp outbreak during an otherwise quiescent time. The outbreak occurred in the Southern hemisphere. There are other equally marked signs of increased activity at times which are close to all the calculated maxima, except that of 1860. This year coincides with a general maximum at which the main and most powerful influence which causes the 11-year period must only be expected to overshadow the weaker periodicity. The year 1894 was one in which the sunspot activity began to show a downward tendency. The most notable spots were noticed in the rotation beginning with May 29, the exact date of the calculated maximum of the period of 4·81 years. Here again the chief spots were in the Southern hemisphere. If we identify the outbreaks in the rotations beginning November 27, 1836, and March 10, 1899, with this particular period, the periodic time is found to be 4·79. I am inclined to think that the evidence of the more accurate observations in the last fifty years is in favour of a period somewhat less than 4·81, but further observations are needed to decide this point. Provisionally, I adopt 4·79 as the most probable time, and $1903{\cdot}72+4{\cdot}79n$ as the most probable date of future maxima.

Table X. may serve to facilitate the further study of this period. It gives the sum of the sixteen columns containing the entries from which the periodicity was deduced. In the original table each entry represented the sum of the mean areas during four successive rotations, and the numbers given here are the sum of fourteen rows, each row corresponding to a period of 4·78 years. The central date of the first entry which fixes the epoch is March 15, 1832, or 1832·203. The amplitude and phase are calculated from the values of $A = +41406$ and $B = -15249$. The phase is found to be $-20° \; 13'$, and this gives the date of the first maximum as $-\frac{20{\cdot}25}{360} \times 4{\cdot}75$, or 0·267 years before the epoch, *i.e.*, in 1831·94.

TABLE X.

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.
44,423	41,514	36,480	37,004	33,806	32,660	30,671	32,407	32,476	38,929	30,881	32,326	43,254	36,576	38,499	47,869
662	598	128	276	445	209	171	23	278	71	313	50	273	298	742	639
3,211	2,117	—	—	—	—	—	—								

The rows to be added in future should be formed as follows: to the first number (44,423) add the sum of the mean daily areas of those four successive rotations, the first of which carries the number 605 in CARRINGTON'S series and begins on December 18, 1898. This number (662) and the following ones completing the first new row have been entered in the table, as well as the two first numbers belonging to the second row. In each new row the number of the first rotation which is taken into account is that included in the expression $605+64n$. If the new set of numbers is treated separately and a change of phase is found to occur, this would indicate a change in the periodic time. For the purpose of estimating the change, the above phase should be considered to belong to the mean point of the interval hitherto treated, *i.e.*, to June, 1865.

12. Although the period of 4·38 does not rest on so secure a basis as the one we have just discussed, it has been very regular in its action during the last five cycles. There have been notable outbreaks of sunspot activity during the rotations 398 (July 4, 1883), 463 (May 11, 1888), 518 (June 19, 1892), 579 (January 8, 1897), and 637 (May 10, 1901), which seem to belong to this period. The maxima take place at dates which may be calculated from the expression $1897{\cdot}00 \pm 4{\cdot}38 \times n$, where n is an integer. Table XI. is constructed similarly to Table X., but as the period does not contain an integer number of four rotations, a certain adjustment in the succession of rows, to prevent a systematic shift of phase, had to be introduced. The row of numbers may, however, now be used to represent the periodicity of the indicated duration, and further rows should be added by beginning each of them

with a sum of four rotations, the first of which coincides most nearly with the date $1897{\cdot}77+4{\cdot}38\,n$.

TABLE XI.

1.	2.	3.	4.	5.	6.	7.	8.
39,998	39,523	33,196	34,432	39,648	37,201	32,956	34,324
1,276	1,688	764	2,179	662	598	128	276
228	150	219	811	579	3,017	1,386	—
9.	10.	11.	12.	13.	14.	15.	—
37,989	41,414	45,278	49,487	42,504	43,543	38,944	—
445	209	171	23	278	71	313	—

The records which have been published since this investigation was first begun enable us to add more than one complete column to those which I have used, and these have been entered in the table.

13. The principal period which gives the present sunspot curve its characteristic shape deserves treatment in detail. Fig. 4 shows the average variation of the six sunspot cycles included between 1833–1899. The curve gives the rise and fall of the annual value of the mean daily area, while the crosses indicate the position of the points through which the curve would pass if deduced from WOLF's sunspot numbers. The close proximity of the crosses to the curve shows that, at any rate as far as the long-period variations are concerned, WOLF's numbers are proportional to the sunspot areas, and that the factor I have used is sufficiently accurate. The figure also illustrates the fact that WOLF's numbers underrate somewhat the activity near the times of a maximum, as has already been pointed out in § 1. But this deficiency is apparent throughout the rising branch of the curve. This points to a systematic difference in the sunspot statistics before and after the maximum. I have carefully examined the sunspot records as far back as the Greenwich records allow me to do so, and there seems indeed to have been a tendency during the 20 available years towards larger average areas (and also average duration) of spots during the rise as compared with the fall in the sunspot cycle. This would explain the deviations of WOLF's numbers from the curve marking the areas.

The general character of the 11-year cycle not coming out with sufficient clearness when only annual averages are taken into account, I have deduced a more detailed curve (fig. 5), basing the calculation on the mean areas obtained during four successive rotations. We notice the sharp rise from the minimum, which takes place about 3½ years before the maximum elevation is reached. The maximum here shows three distinct peaks, and although their position may vary in the individual maxima, the sharp secondary rise and fall of the activity in the time immediately following a maximum is characteristic. The temporary recovery of activity about 3 years after the maximum is also a feature which may often be traced in the separate cycles.

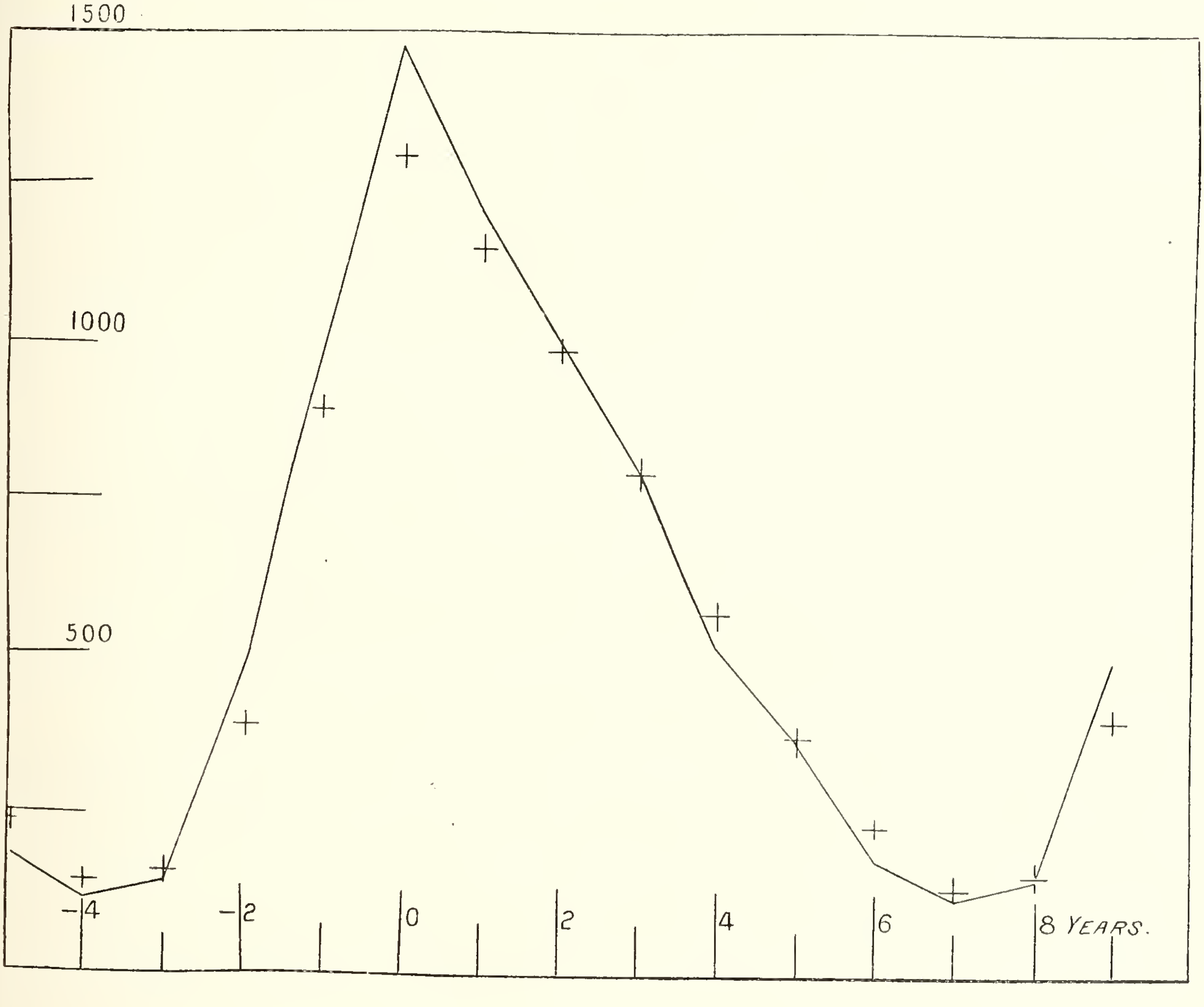

Fig. 4.

I have investigated the sub-periods as well as the main 11-year period, taking the measurement of areas (publication *b*) as basis. Table XII. gives the results. It will be noted how closely the phase of the main period agrees with that derived in § 4 from WOLF's numbers.

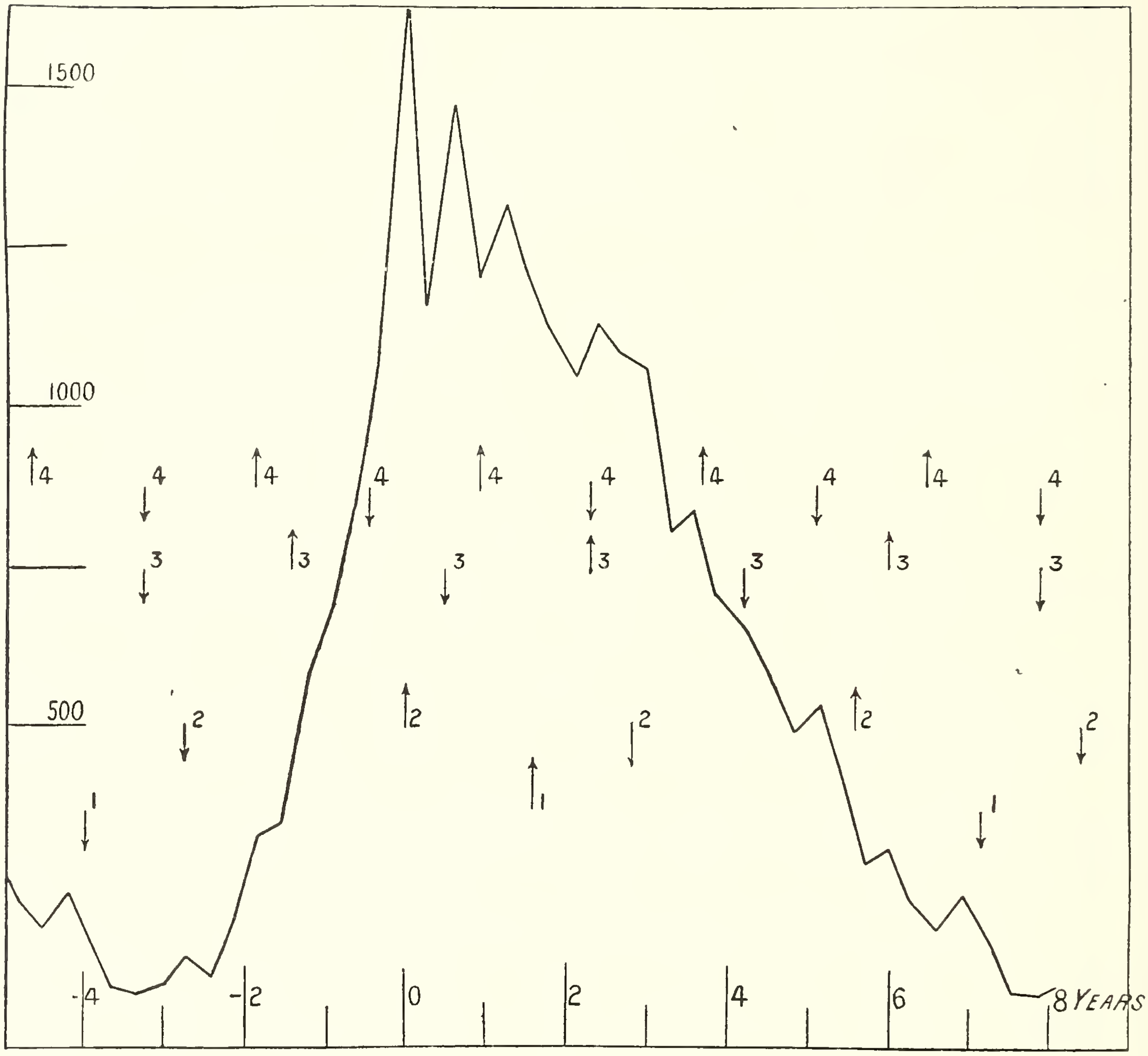

Fig. 5.

TABLE XII.

Period in years.	Amplitude (mean daily areas).	Ratios of Amplitudes.	Dates of maxima.
11·12	586	1	$1905 \cdot 35 \pm 11 \cdot 12 \times n$
$\frac{1}{2} \times 11 \cdot 12$	142	0·242	$1903 \cdot 75 \pm \frac{1}{2} \times 11 \cdot 12 \times n$
$\frac{1}{3} \times 11 \cdot 12$	64	0·109	$1902 \cdot 35 \pm \frac{1}{3} \times 11 \cdot 12 \times n$
$\frac{1}{4} \times 11 \cdot 12$	50	0·085	$1904 \cdot 66 \pm \frac{1}{4} \times 11 \cdot 12 \times n$

The highest point of the complete curve is reached at a time $1903{\cdot}76 \pm n \times 11{\cdot}12$, but there is naturally a good deal of uncertainty as to the dates of the maxima, within the limits of a year. The positions of the maxima and minima of the harmonic components as given in Table XII. are marked in fig. 5 by an upward arrow denoting a maximum and a downward arrow a minimum. The order of the harmonic is indicated by the figures attached to the arrows. A retardation of 18 months in the principal maximum may occur owing to the temporary disappearance of the first harmonic, and does not therefore necessarily indicate an irregularity in the main periodicity.

The discussion of the 11·125 years' period has been entirely based on the results of the last 75 years of last century. Between 1749 and about 1826 the periodogram only gives a faint indication of the period. This remnant I ascribed at first without further investigation to the fact, that the 11 years' period had come into life towards the beginning of the century, and therefore had to some extent affected the interval 1750–1826 to which curve B of fig. 2 applies. This was an error which for some time kept me off the right track.

The question of the permanence of the periodicities is one of vital importance, and I have endeavoured throughout to keep my mind free from all preconceived notions. Every one thus looking with unprejudiced eyes at the main facts must feel himself drawn in opposite directions. On the one hand there is the evidence of the periodogram which indicates almost decisively a new departure at the beginning of the nineteenth century; on the other hand we have the remarkable fact that WOLFER, making use of all the data since 1610, deduced 11·124 years as the most probable period—a result identical with mine. Similarly NEWCOMB,* after a most careful examination of the same records, arrives at a period of 11·13 years. It needs to be explained why the years in which, according to our results, the periodicity was apparently absent do not affect the mean duration of the period, so that the same value is obtained whether the time during which the periodicity is *ex hypothesi* absent is included in the calculations or not. My first impression was that the coincidence was partly a matter of accident and partly due to the fact that both observers attached weights to the times of the observed maxima according to their trustworthiness. The weights thus attached to the records of the last 70 years naturally much exceeded those with which previous records were credited. Hence the whole result might very well be found to depend on the later periods only. When first writing out the account of my work, this was the view I took, and it was only very gradually that I abandoned it. I am convinced now that it is untenable.

To put the reader into possession of all the facts, and to get at a clear view of the subject, it seems advisable to state in detail the arguments which seemed to point to the conclusion that the 11 years' period was only of recent origin. In Table XIII. the first column contains the times of sunspot maxima as copied from WOLFER's tables. The third column contains the intervals between two successive maxima. The fourth gives the sum of four successive intervals. Starting with the last figure so as to make use of all the best determined maxima, the first must be omitted when the intervals are collected in groups of four. It will be noticed that the average interval of four periods is approximately constant from 1675 to 1848, or during a period of over 170 years; the average of the periods which took place during that time is consistently about 10·8 years. It follows that, independently of the observations in the last 60 years, it is only the long intervals between 1626 and 1675 which bring up the average to 11 years. The latter part of this interval was one of great scarcity of sunspots, very few being observed between 1640 and 1670, and the whole of the second part of the seventeenth century seems to have been quite anomalous, as regards the behaviour of spots.*

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* 'Astrophysical Journal,' vol. 13, p. 1 (1901).

TABLE XIII.

Maxima.	Δ.	Interval.	Sums of four successive intervals.	Maxima.	Δ.	Interval.	Sums of four successive intervals.
1615·5	−0·8	—	—	1761·5	+1·0	11·2	43·3
1626·0	−1·4	10·5	—	1769·7	−1·9	8·2	—
1639·5	+1·0	13·5	—	1778·4	−4·2	8·7	—
1649·0	−0·6	9·5	—	1788·1	−5·6	9·7	—
1660·0	−0·6	11·0	—	1805·2	+0·4	17·1	43·7
1675·0	+3·3	15·0	49·0	1816·4	+0·5	11·2	—
1685·0	+2·2	10·0	—	1829·9	+2·9	13·5	—
1693·0	−0·9	8·0	—	1837·2	−0·9	7·3	—
1705·5	+0·5	12·5	—	1848·1	−1·1	10·9	42·9
1718·2	+2·1	12·7	43·2	1860·1	−0·2	12·0	—
1727·5	+0·3	9·3	—	1870·6	−0·8	10·5	—
1738·7	+0·4	11·2	—	1883·9	+1·4	13·3	—
1750·3	+0·9	11·6	—	1894·1	+0·5	10·2	46·0

[The assumed grouping is admittedly arbitrary, but serves to show how difficult it is to devise a satisfactory measure of a period from the observations of maxima which are unequally spaced.—*February* 18, 1906.]

Assuming the permanency of the 11 years' period, both NEWCOMB and WOLFER formed tables giving the deviation in time of the observed maxima with those of a mean period derived from the whole of the available material. These deviations, according to WOLFER's estimate, are given in the second column of Table XIII. It will be seen at once that though differences occur amounting in one case to 5·6 years, yet the maxima seem on the whole to group themselves in pretty close proximity to the calculated times. Professor NEWCOMB sums up his conclusions in the sentence :—

"Underlying the periodic variations of spot activity there is a uniform cycle, unchanging from time to time, and determining the general mean of the activity."

A convincing feature of the second column of Table XIII. is that when maxima such as those of 1727, 1738, 1750, and 1761 are at a distance of nearly 11 years, the differences between the calculated and observed times are always small. The two maxima of 1649 and 1660 fit in well in a similar manner with the computed times. These facts are difficult to explain unless we believe in the permanency of the period. Having thus once more become a partial convert to that belief, I turned again to the periodogram of 1750 to 1826 (curve B, fig. 2). The small peak showing at $11\frac{1}{4}$ years I had, as explained, ascribed to the years 1800–1826, during which, as I then thought, the 11-year period had come into existence. In order to clear up the matter, I investigated separately the five cycles between 1749 and 1794. The 11 years' oscillation now came out with an amplitude of 256, rather larger than I expected (the present amplitude being 586), and the phase was such as to give a maximum in 1747·5. A period of exactly $11\frac{1}{8}$ years would bring us after thirteen cycles to about 1903·1, agreeing to about two years with the actual date of the maximum of the 11-year period, as given in Table XII.

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* According to SPORER there is no record of a sunspot being seen on the Northern Hemisphere of the Sun between 1672–1705.

[Not much value can be attached to the phase calculated from five periods only at a time, when we know that other and stronger influences were at work. The conclusion to be drawn is that even when the periodicity in question was weak, its phase was not inconsistent with that calculated from other intervals of time.—*February* 18, 1906.]

The result reached at this point was that the 11 years' period though diminishing occasionally in intensity was yet permanent throughout the range of available sunspot records, and that whenever the time of successive maxima was nearly equal to 11 years they fitted in well with each other as regards phase.

14. Let us follow up the suggestion furnished by the last remark. Notice that during the three centuries to which Table XIII. applies there were three cases in which the interval between two successive sunspot maxima was nearly 13·5 years. Table XIV. shows that the intervals between each of these three single periods is nearly a multiple of the same duration, so that all figures fit in with a general periodicity of about 13·6 years.

TABLE XIV.

Sunspot maxima.	Length of period.	Intervals between periods.
1626 1639·5	13·5	
—	—	1816·4 − 1639·5 = 176·9 = 13 × 13·61.
1816·4 1829·9	13·5	
—	—	1870·6 − 1829·9 = 40·7 = 3 × 13·57.
1870·6 1883·9	13·3	
—	—	1883·9 − 1626 = 257·9 = 19 × 13·57.

It should be noted that the first of the intervals of 13·5 years occurred previous to 1649, and is not brought into the calculation of the periodogram, which shows a decided maximum (fig. 1) for a period of 13·5 years. This period has evidently been one of the characteristic ones during the time to which curve B (fig. 2) applies. The fact that the maxima 1870·6 to 1883·9 are connected with it shows that it has still been active till quite lately. If it does not appear in curve A (fig. 2), this is accounted for by the fact that the first diffraction band of the 11 years' period overlaps and neutralises it. When the large period is eliminated, a rise at about 13 years becomes apparent. The process of elimination is, however, difficult, and errors may easily be introduced by means of it. There is evidence of two overlapping periods here, the broadness of the rise in curve B (fig. 2) being one of the indications of the duplicity. I refrain for the present, therefore, from discussing the period further.

15. Having found the average action of the $11\frac{1}{8}$ years' period, we may eliminate it from the general sunspot curve. The result is shown in fig. 6, in which the annual values of sunspot areas since 1833 (publication *b*) has been used. The process of elimination brings out a period of about 8·5 years in a striking manner. The maxima occurred in the years 1836, 1845, 1853, 1862, and 1870. The periodogram for the combined interval 1749 to 1900 shows a maximum at the period of 8·25 years. Taking the phase as obtained by means of the 8·25 years' oscillation from the interval 1749 to 1826 alone, and forecasting the maxima for the subsequent interval, we obtain 1836·1, 1844·5, 1852·7, 1861·0, and 1869·2, in almost exact agreement with the above. In fig. 6 short lines are drawn indicating the maxima of the curve, while arrows mark the positions of the maxima calculated, as first explained, from the observations which are not included in the time scale of the figure.

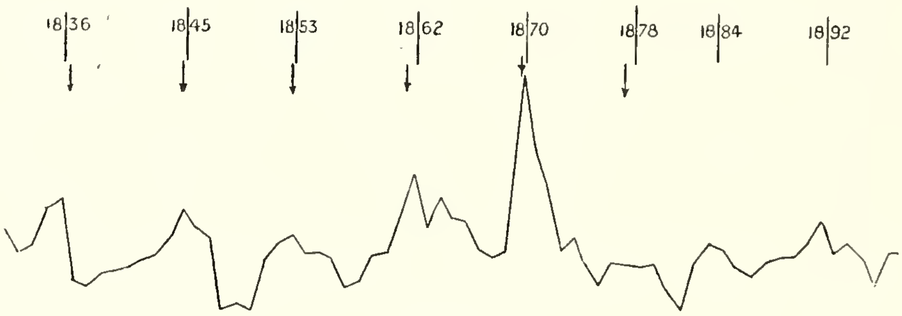

Fig. 6.

The phases of the 8·25 years' period, as calculated from the two intervals separated by nine periods, are given in Table IV., and are there found to differ by 26°. When minutes of arc are taken into account, this angle is more accurately found to be 25° 16′. To bring the phases into coincidence, the period would have to be slightly lengthened, so as to be equal to 8·31 years. If we start from the 8·5 years' oscillation, we find similarly a diminution of phase equal to 34° 5′, and the period calculated so as to destroy this difference would be 8·41 years. We may adopt the mean of these results and take 8·36 as the most probable period. To get the phase we may use the method explained in § 4, which leads to the results given in Table XV. For each period we obtain three numbers according as we use the whole interval or the two separate halves.

TABLE XV.

Period.	Calculated phases of 8·36-year period.		
	1749–1900.	1749–1826.	1826–1900.
7·5	353°	210°	340°
7·75	—	215	199
8	191	196	173
8·25	198	207	190
8·5	217	201	221
8·75	278	229	140

It will be noticed that, except as regards the values derived from the shortest and longest periods included in the table, the phases are concordant. The amplitude of this period being only about one-third of that of the 11 years' period, it is more likely to be interfered with by accidental variations, and therefore a closer agreement cannot be expected. We may take 206° as the most probable phase, which, converted into years, gives 1904·51±8·36n as the dates of the maxima of this period. It is significant that there are maxima with identical phases for the semi-period of 4·125

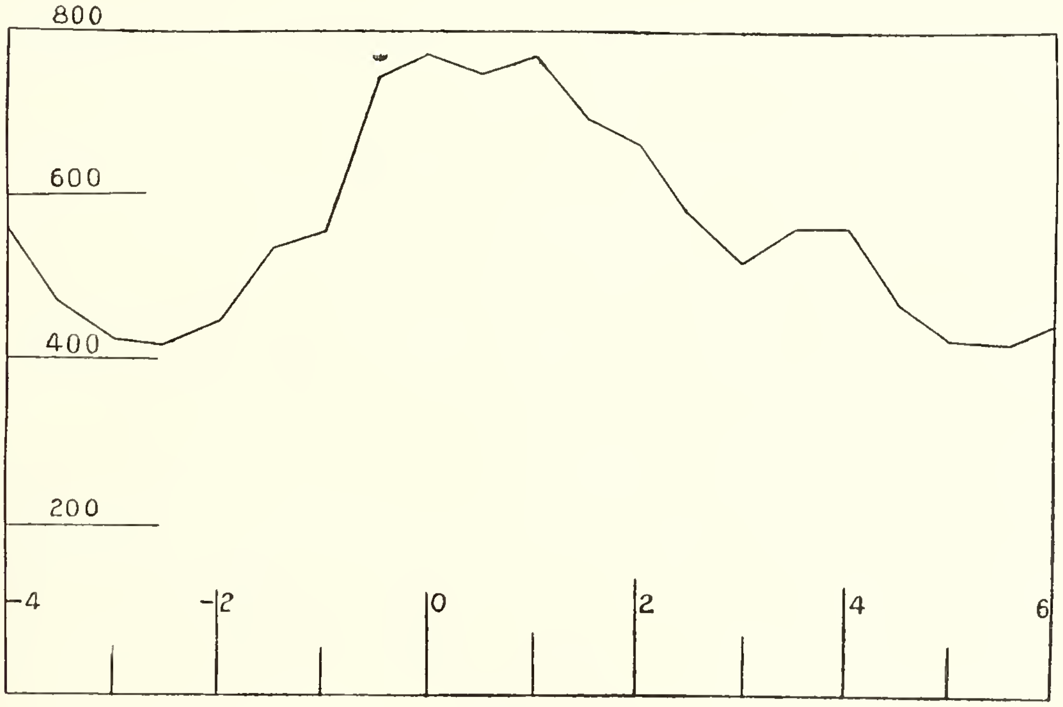

Fig. 7.

years in the two portions of the time interval (see Table III.). This period wants further careful study. The rise and fall of the sunspot curve during the 8-year cycle is shown in fig. 7, which is based on WOLF's numbers, making use of all observations since 1749.

16. We have now ascertained the existence of at least four periods, three of which have been determined with considerable accuracy. Their periodic times are 4·80, 8·36, and 11·125. Taking frequencies into consideration in place of periodic times, we are led to consider reciprocals and thus find

$$\begin{aligned} (11{\cdot}125)^{-1} &= 0{\cdot}08989 \\ (8{\cdot}36)^{-1} &= 0{\cdot}11962 \\ \hline \text{Adding up, we find } (4{\cdot}77)^{-1} &= 0{\cdot}20951 \end{aligned}$$

Hence the sum of the frequencies of two of the periods agrees within the limits of possible errors with the frequency of the third period. This relationship suggests an origin of the 4·8 years' variation, which may be similar to the origin of the vibrations of sound which go by the name of combination tones. Two causes varying as $\cos n_1 t$ and $\cos n_2 t$ respectively give rise, if the effect depends partly on the higher powers of the cause, to oscillations varying as $\cos (n_1+n_2)t$ and $\cos (n_1-n_2)t$. The corresponding time of the second combination tone would be 33·38 years.

But it is also found that the two first numbers are very nearly in the ratio of three to four, so that we may also express the three periodic times as sub-periods of 33·375 years, thus:

$$\begin{aligned} \tfrac{1}{3}\times 33{\cdot}375 &= 11{\cdot}125 \\ \tfrac{1}{4}\times 33{\cdot}375 &= 8{\cdot}344 \\ \tfrac{1}{7}\times 33{\cdot}375 &= 4{\cdot}768 \end{aligned}$$

How far this connexion is accurate or approximate is impossible to say at present, but the fact that the three periods which have been traced with certainty should also bear a remarkably simple relationship to each other is worthy of note.

The question naturally occurs whether the great difference in sunspot activity observed when different maxima are compared with each other may be accounted for by the overlapping of different periods which sometimes will strengthen and sometimes weaken each other's effects. That the difference is not exclusively due to such overlapping is proved by the evidence of the periodogram, which for instance teaches us that in the second part of the eighteenth century the 11-year period was reduced to a fraction of its normal value.

Nevertheless it is true that in the exceptionally great outburst in 1870 nearly all the periods found seem to have been at their maximum phase. Similarly in the great outbreak of 1837 all but the 13·5-year period agreed in phase. This is shown by Table XVI.

TABLE XVI.

Period.	Calculated maximum.	Calculated maximum.	Principal outbreaks.
4·38	1870·7	1835·7	1836·9 1837·5 1837·9
4·80	1870·4	1836·7	
8·36	1871·1 [1869·2]	1837·6 [1836·1]	1870·2 1870·4 1870·7 1871·3
11·125	1870·4 1872·0	1837·0 1838·6	
13·5	1870·0 [1871·4]	—	—

Of the two numbers given for the 11-year period the first refers to the observed maximum of the total oscillation which includes the harmonics, while the second gives the maximum phase of the fundamental period. The last column gives the dates of the principal outbreaks which together make up the two maxima concerned.

The significance of the table may be thought to be weakened to some extent by the consideration that the two exceptional maxima of 1837 and 1870 make themselves felt in the numerical reductions, tending to attract the maximum of any periodicity towards themselves. I have therefore for the two periods of 8·3 and 13·5 years added in brackets the dates of the maxima calculated from observations which all were previous to 1826, and which could not be affected in this manner.

17. The general conclusion arrived at brings us, I think, a decided step nearer to the solution of the problem of sunspot periodicities. The existence of a number of definite periods cannot be doubted, whatever we may think of their numerical relationship. The recurrence of the maximum activity of each period seems to take place with an accuracy which may be equal to that of orbital revolution, but the characteristic property of these periods is the great variability of the activity. To this variability we must attribute the cause why the periodicities have been allowed to remain hidden for so long a time. If we associate the periods, as seems natural, with the existence of meteor streams, these streams must vary in the power of setting up the disturbance which is the ultimate cause of the formation of a spot. I have for a long time believed in, and occasionally expressed, the opinion that sunspots are only secondary phenomena consequent on disturbances in the immediate surroundings of the sun, which are due to a general increase of electric conductivity affecting a great portion of interplanetary space. Such change in electric conductivity could be brought about by meteoric swarms fertilised by ionized matter which they have picked up in their journey through space.

The answer to many questions which naturally occur can only be given when further observations are available. But the existing material has not yet been exhausted, and may be expected to give further results, which I hope to present to the Society in due course.

TABLE I.—Comparison of Areas and WOLF'S Sunspot Numbers.

Year.	Mean daily area for each year.	WOLF'S sunspot numbers.	Ratio.	Year.	Mean daily area for each year.	WOLF'S sunspot numbers.	Ratio.
1832	274	27·5	9·96	1867	131	7·3	17·95
1833	60	8·5	7·06	1868	434	37·3	11·63
1834	133	13·2	10·08	1869	972	73·9	13·15
1835	773	56·9	13·58	1870	2761	139·1	19·36
1836	1331	121·5	10·96	1871	2004	111·2	18·02
1837	1170	138·3	8·46	1872	1462	101·7	14·38
1838	903	103·2	8·75	1873	766	66·3	11·55
1839	780	85·8	9·09	1874	601	44·7	13·45
1840	586	63·2	9·27	1875	272	17·1	15·91
1841	348	36·8	9·46	1876	122	11·3	10·80
1842	254	24·2	10·50	1877	92	12·3	7·48
1843	95	10·7	8·88	1878	19	3·4	5·59
1844	171	15·0	11·40	1879	30	6·0	5·00
1845	419	40·1	10·45	1880	402	32·3	12·45
1846	626	61·5	10·18	1881	679	54·3	12·50
1847	1021	98·5	10·36	1882	1002	59·7	16·78
1848	986	124·3	7·93	1883	1155	63·7	18·13
1849	765	95·9	7·98	1884	1079	63·5	16·99
1850	494	66·5	7·43	1885	811	52·2	15·53
1851	683	64·5	10·59	1886	381	25·4	15·00
1852	545	54·2	10·06	1887	179	13·1	13·67
1853	436	39·0	11·18	1888	89	6·8	13·09
1854	113	20·6	5·49	1889	78	6·3	12·38
1855	64	6·7	9·55	1890	99	7·1	13·94
1856	49	4·3	11·40	1891	569	35·6	15·99
1857	201	22·8	8·82	1892	1214	73·0	16·63
1858	714	54·8	13·03	1893	1464	84·9	17·25
1859	1404	93·8	14·96	1894	1282	78·0	16·44
1860	1172	95·7	12·25	1895	974	64·0	15·22
1861	1258	77·2	16·29	1896	543	41·8	12·99
1862	1363	59·1	23·06	1897	514	26·2	19·62
1863	702	44·0	15·95	1898	375	26·7	14·05
1864	784	47·0	16·68	1899	111	12·1	9·17
1865	407	30·5	13·35	1900	75	9·5	7·90
1866	318	16·3	19·51	1901	29	2·7	10·74

TABLE IV.—Intensity and Phase of Periodogram.

I. Period in years.	II. 1750–1900.	III. 1750–1826.	IV. 1826–1900.	V. Beginning of second period.	VI. 1750–1900.	VII. 1750–1826.	VIII. 1826–1900.
24	48×10^3	42×10^3	13×10^3	1821	267°	259°	280°
23	17	59	3	1818	292	285	320
22	112	83	102	1815	239	288	208
21	349	198	191	1812	314	317	312
20	298	430	48	1809 (I)	4	352	32
19	35	147	174	1825	93	14	156
18	9	238	291	1821 (I)	295	42	235
17	83	224	38	1817	60	91	344
16	278	228	123	1813 (I)	164	186	139
15·5	340	304	91	1811 (I)	234	236	230
15·25	436	319	136	1825 (I)	238	238	237
15	434	394	117	1824 (I)	271	259	293
14·75	432	598	68	1822 (II)	296	282	342
14·5	342	755	6	1821 (II)	307	302	64
14·25	474	1058	36	1820 (I)	313	323	211
14	278	1122	40	1819 (I)	338	339	164
13·75	550	1337	6	1817 (II)	356	0	266
13·5	696	1170	33	1816 (II)	16	17	10
13·25	552	1150	77	1815 (I)	55	39	122
13	198	946	312	1814 (I)	100	57	191
12·75	21	788	517	1825 (II)	118	87	259
12·5	105	584	1019	1824 (I)	3	112	317
12·25	675	345	1526	1822 (II)	65	148	37
12	1464	289	2302	1821 (I)	125	185	107
11·86	1951	—	—	1820 (I)	155	—	—
11·75	2338	322	2894	1819 (II)	192	237	180
11·5	3700	465	3839	1818 (I)	253	265	250
11·25	4230	701	4396	1816 (II)	326	297	335
11	2724	605	4541	1826 (I)	31	325	50
10·75	742	793	3774	1824 (I)	122	349	142
10·5	853	877	3202	1822 (II)	251	356	221
10·25	2026	1179	1842	1820 (II)	337	16	306
10	1677	1475	440	1819 (I)	27	22	35
9·75	1050	1818	84	1817 (I)	60	49	107
9·5	1313	2017	156	1825 (I)	75	62	129
9·25	603	2050	440	1823 (I)	120	94	226
9	364	1885	257	1821 (I)	97	114	322
8·75	812	1390	142	1819 (I)	135	153	282
8·5	770	743	185	1825 (II)	163	174	140
8·25	933	486	495	1823 (I)	241	228	254
8	177	374	404	1821 (I)	336	266	30
7·75	—	402	269	1811 (I)	—	334	201
7·5	264	371	22	1824 (I)	18	25	345
7·375	173	—	—	—	63	—	—
7·25	106	264	34	—	54	74	318
7·125	149	—	—	—	94	—	—
7	99	68	82	—	158	116	188
6·875	18	—	—	—	317	—	—
6·75	52	7	61	—	55	94	44
6·625	49	—	—	—	124	—	—
6·5	1	24	25	—	192	64	231
6·375	7	—	—	—	145	—	—

Table IV.—Intensity and Phase of Periodogram (continued).

I. Period in years.	II. 1750–1900.	III. 1750–1826.	IV. 1826–1900.	V. Beginning of second period.	VI. 1750–1900.	VII. 1750–1826.	VIII. 1826–1900.
6·25	5 × 10³	23 × 10³	13 × 10³	—	28°	76°	295°
6·125	24	—	—	—	62	—	—
6	102	24	136	—	154	105	173
5·93	54	—	—	—	202	—	—
5·875	122	—	—	—	293	—	—
5·75	236	3	397	—	63	346	68
5·625	128	55	420	—	249	35	239
5·5	224	62	259	—	37	78	18
5·375	129	—	—	—	160	—	—
5·25	15	28	33	—	238	174	295
5·125	31	—	—	—	286	—	—
5	12	44	2	—	305	310	147
4·875	97	152	14	—	7	21	321
4·75	99	170	49	—	86	56	153
4·625	70	132	8	—	108	122	33
4·5	25	56	2	—	159	173	79
4·375	41	41	19	—	305	278	341
4·25	9	59	14	—	355	341	145
4·125	109	81	34	—	54	57	50
4	29	57	33	—	25	73	323
3·875	—	12	6	—	—	0	227
3·75	24	14	41	—	89	22	121
3·67	—	—	61	—	—	—	5
3	—	1	2	—	—	—	—

Table V.—Intensity of Periodogram 5·18–1·89 years.

I. Period in years.	II. Intensity of periodogram.	I. Period in years.	II. Intensity of periodogram.	I. Period in years.	II. Intensity of periodogram.
5·18	23 × 10³	3·78	121 × 10³	2·49	1 × 10³
5·08	10	3·69	75	2·44	13
4·98	51	3·59	18	2·39	21
4·88	133	3·49	22	2·34	14
4·78	167	3·39	13	2·29	19
4·68	105	3·29	5	2·24	17
4·58	15	3·19	6	2·19	26
4·48	47	3·09	29	2·14	39
4·38	123	2·99	1	2·09	21
4·28	79	2·89	16	2·04	30
4·18	29	2·79	46	1·99	16·1
4·08	43	2·69	49	1·94	54·2
3·98	7	2·59	43	1·89	25·3
3·88	39	2·54	11		

Table VI.—Intensity of Periodogram for Periods of 2·240 years to 55 days.

Period.	Intensity.	Mean intensity.	Period.	Intensity.	Mean intensity.	Period.	Intensity.	Mean intensity.
Years.			Years.			Days.		
2·240	87	310×10^2	1·120	81	137×10^2	136	523	163×10^2
	72			24			12	
	1059			432			34	
	30			10			16	
2·090	53	290	1·045	29	198		366	
	17			44			27	
	832			499		116	27	45
	257		Days.	218		(Mercury)	19	
1·941	17	230	354·5	11	181		142	
	194			343			6	
	583			204			42	
	127			168			32	
1·792	106	131	327·24	423	367	109	366	116
	221			561			27	
	160			291			108	
	38			192			6	
1·642	113	204	299·97	409	188		99	
	99			154			90	
	141			65		68	172	90
	463			124			15	
1·599	297	240	291·92	109	42		106	
(Venus)	171			26			10	
	27			2			138	
	464			33			93	
1·568	159	132	286·33	2	63	58	192	81
	127			117			12	
	60			103			130	
	180			32			19	
1·493	48	120	272·7	8	167		0	
	205			291			129	
	91			338		55	1006	181
	138			33			1	
1·344	359	185	245·4	124	147		12	
	7			96			15	
	304			309			42	
	69			58			10	
1·195	355	199	218·16	7	179			
	45			126				
	175			579				
	223			6				

TABLE VII.—Intensity of Periodogram for Periods of 30–13·3 days.

Period in days.	1886–1890.	1890–1895.	1895–1900.	Mean.	General average.
30	840	8	13,560	4,800	12,400
29	830	12,970	15,240	9,680	
28	600	64,470	3,050	22,710	
27·27	7,640	21,930	410	9,990	10,240
27	2,210	50,610	2,550	18,460	
26·5	2,990	1,800	2,000	2,260	
26	1,430	83,150	3,860	29,480	11,440
25	240	6,370	4,640	3,750	
24	1,130	670	1,440	1,080	
15	170	1,500	220	630	520
14·5	280	1,150	570	670	
14	100	380	270	250	
13·635	300	850	70	410	1,210
13·5	270	2,090	50	800	
13·25	100	5,850	1,320	2,430	
13	100	480	710	430	360
12·5	50	3	760	270	
12	240	30	850	370	
13·298	—	—	—	3,080	
13·296	—	—	—	2,150	

TABLE VIII.—Intensity of Periodogram, Values of A and B, and Phases of the 26- and 27-day Periods for Separate Years.

Year.	Period of 26 days.	Period of 27 days.	A.		B.		ϕ.	
			26 days.	27 days.	26 days.	27 days.	26 days.	27 days.
1886	376×10^2	856×10^2	− 24627	− 40513	− 12679	+ 12973	207°	162°
1887	157	169	+ 5292	− 16363	+ 17068	+ 8062	73	154
1888	26	17	+ 1	+ 5934	+ 7222	− 128	90	359
1889	75	58	− 3426	+ 7075	− 11855	− 8062	254	311
1890	36	82	− 7821	+ 10934	− 3535	− 7274	204	326
1891	1024	994	+ 12457	+ 16437	− 43946	− 41146	286	292
1892	1376	407	+ 29666	− 29218	− 43865	+ 2340	304	175
1893	1202	2899	+ 4419	+ 4639	− 49310	− 75526	275	274
1894	2854	1445	+ 74603	− 54639	+ 15907	− 8310	12	189
1895	2007	3645	+ 37343	+ 60644	− 51933	− 59345	306	316
1896	62	279	− 11514	+ 11137	+ 1570	− 21563	172	297
1897	268	372	− 22851	+ 13126	− 4903	+ 23705	192	61
1898	901	144	+ 1208	+ 333	+ 42845	− 17454	88	271
1899	13	14	+ 3968	+ 4230	− 3408	− 3062	319	324
1900	67	53	+ 6396	+ 902	+ 9800	− 10532	57	275

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IONIC SIZE IN RELATION TO THE PHYSICAL PROPERTIES OF AQUEOUS SOLUTIONS

BY

W. R. BOUSFIELD, M.A., K.C.

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By W. R. BOUSFIELD, *M.A., K.C.*

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PART I.—INTRODUCTION.

THE electrical conductivity of a solution depends upon the rates of transference of the ionised portions of the solute in opposite directions under the influence of the applied electro-motive force. These rates of transference under a given potential gradient are conditioned by the viscosity of the medium and the sizes and possibly the shapes of the ions. Increase of viscosity of the solution and increase in the sizes of the migrating ions both tend to diminish the rates of transference of the ions, and thus to lower the conductivity. If the ion enters into combination with one or more molecules of water, its size is necessarily increased, and the motion of the water-logged ion becomes more sluggish as the amount of water in combination increases. To separate the elements which determine the conductivity of an electrolytic solution, and to analyse the joint effect of variations in ionisation, viscosity and water combination is a matter of great difficulty, but of much importance to the theory of solution.

In a former paper (BOUSFIELD on "Ionic Sizes in Relation to the Conductivity of Electrolytes"*) was proposed a method for effecting such an analysis based upon the expression evaluated by STOKES for the terminal velocity of a small sphere moving in a viscous medium. A consideration of the influence of the water in combination with the ion upon its mobility was used to obtain a correction of the coefficient of ionisation, which made VAN 'T HOFF's law (in a slightly modified form) an *accurate* expression of the relation between ionisation and dilution, down to twice decinormal solutions of KCl. This method of procedure gave for the radius of the hydrated ion an expression of the form

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* Communicated to the Royal Society, February 10, 1905. Revised and published in the 'Zeit. für Phys. Chem.,' 53, 257, 1905. (See *infra*, Part VIII., p. 153.)

$$r = r_{\infty}(1+Bh^{-2/3})^{-1},$$

which indicated that the average radius of the ion steadily increased with dilution, owing to increasing hydration of the ion, up to "infinite dilution." Whether the resulting expression for r did in fact represent the average radius of the ion was tested by a consideration of the density law which would thence result. The volumes of the ions would be proportional to r^3, and it was found that a rational density formula could be constructed upon this basis which accurately corresponded with the observed densities of the solutions.

In the present paper the necessary experimental determinations for applying the method to solutions of NaCl are given, together with some other determinations for collateral purposes, and the hypothesis is further tested by reference to other physical properties of solutions. These results are independently of some value, apart from the hypothesis by which they are reached, and it has been thought well to designate the function r, which, according to our view, expresses the average radius of the ion, by the term "radion." Whilst this term connotes our hypothesis, it may, if necessary, be merely considered as expressing a certain function of the dilution. But it has a further convenience, as it enables us readily to extend the conception to denote the average molecular radius of any group of ions or molecules, or even of the whole of the ions and molecules both of solvent and solute in any given solution. The utility of this extended conception will appear more clearly in the section relating to a consideration of ionic size with reference to the viscosity of a solution.

The volume of the ion, according to our hypothesis, is proportional to the cube of the radion, and the volume of a pair of ions to the sum of the cubes. These cubes and their sums we refer to as "ionic volumes." But except where the context indicates the contrary, the term "radion" may be taken as merely denoting the function

$$r = r_{\infty}(1+Bh^{-2/3})^{-1},$$

and the term "ionic volume" as denoting the cube of the radion or sum of the cubes of the radions, apart from the hypothesis as to size.

As in our former paper, with reference to KCl, it is shown that the "solution volume" of NaCl solutions is a linear function of the ionic volumes. Hence the densities of KCl and NaCl solutions can both be accurately expressed by the same formula as simple functions of the radions.

A theoretical consideration of the relation of the Hittorf migration numbers to the sizes of the ions is given, and it is shown that our hypothesis as to the influence of ionic sizes upon rates of transference would theoretically lead to the result that the reciprocals of the Hittorf migration numbers should be expressible as a linear function of the ratio of the radions. This turns out in fact to be the case, and we incidentally arrive at a useful method of extrapolation to determine the value of the Hittorf number for an electrolyte at "infinite" dilution.

These considerations enable us to determine the coefficients B for the separate ions in the expressions for the radions. These coefficients B we refer to as the "hydration numbers," the relation between the hydration numbers and the migration numbers at infinite dilution being of the form

$$B = B_1N_1 + B_2N_2.$$

Turning now to a consideration of the viscosities of the KCl and NaCl solutions, it is shown that the viscosity of these solutions can be represented approximately as a linear function of the radions, as can also the viscosity of mixtures of normal KCl and NaCl solutions.

Passing to a consideration of the general relation of viscosity to ionic size, the extended conception of the radion is introduced, and an approximate value is given to the radion of water, which expresses the average radius of the water molecules reckoned upon the same scale as the radions of the solute. Using this value of the water radion in conjunction with the values of the radions of the solute determined from the conductivities, it is shown that the viscosity of the solutions can be expressed with a fair approach to accuracy by the expression

$$\eta = C\Sigma\beta r,$$

where r stands for the radion of a given species of molecules, and β for the fraction of the total volume occupied by such species. Since $\Sigma\beta r$ is, upon the extended conception of the radion, the average molecular radius of the whole solution, we may express this result by saying that the viscosity of an aqueous solution is proportional to its radion.

In order to correlate ionic sizes with osmotic pressure, a prolonged attempt was made to measure the vapour pressure of dilute KCl solutions at 18° C. A large barometer tube was used, closed by a small tap at the bottom, so that minute differences of level could be determined by removing and weighing the mercury cistern. A similar arrangement was used to determine simultaneously the variations of atmospheric pressure during each observation. It was found, however, that the variations of atmospheric pressure were often larger than the differences of vapour pressure to be measured, and no sufficiently accurate results could be obtained. Recourse was therefore had to the freezing-point determinations of JAHN with KCl and NaCl solutions. The variations of ionic size with temperature are probably serious and at present* unknown, and hence a consideration of ionic sizes at 18° C. in relation to osmotic data at another temperature might lead to error. But it seemed probable that the ionic sizes at different dilutions might have the same *relative* values at 18° C. and 0° C., and in the absence of other data it was decided to use these.

Defining the "effective molecular freezing-point depression" as the ordinary so-called molecular freezing-point depression divided by $(1+\alpha)$, where α is the ionisation, and denoting it by the letter D, it was found that D was a linear function of the ionic volume, and that it could be expressed both for KCl and NaCl as

$$D = 1{\cdot}86 + C\,(I_{\alpha} - I_{v}),$$

where I_v stands for the ionic volume at the given dilution and I_{α} for the ionic volume at infinite dilution, the value of the constant C being nearly the same for both substances.

In addition to the confirmation thus afforded to our view as to the fundamental importance of the radion in the theory of solutions, we are further led to a useful formula for obtaining by extrapolation the value of the molecular freezing-point depression at "infinite" dilution. For this purpose we are able to dispense with our hypothesis, and obtain from it a new result quite independent of it—one of the recognised tests of the validity of a hypothesis, though not a conclusive one.

We saw that the solution volume was a linear function of the ionic volume, and we have now the effective molecular freezing point-depression also as a linear function of the ionic volume. Hence the effective molecular freezing-point depression should be a linear function of the solution volume, and in this case the reference to ionic sizes which correlated the two sets of phenomena can be dispensed with. In order to test this matter, measurements of the densities of KCl and NaCl solutions at 0° C. were made. This is a little above the freezing point of dilute solutions, but it was considered to be near enough to make the desired comparison. Density measurements were made upon solutions of strengths of $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, $\frac{1}{16}$, $\frac{1}{32}$ normal, and empirical formulæ (based on the lines of the rational formulæ for 18° C.) were constructed to obtain the solution volumes at the concentrations at which JAHN'S freezing-point determinations were made.

The result was that the effective molecular freezing-point depression both for KCl and NaCl solutions could be expressed by one formula with the same constants for both substances, viz. :—

---

* In my former paper I attempted to calculate the variation of ionic size with temperature by reference to the conductivity temperature coefficients of the ions at infinite dilution which were given by KOHLRAUSCH. I have, however, since come to the conclusion that these results are unreliable. KOHLRAUSCH'S values were largely based on determinations of the conductivities of $\frac{1}{1000}$ normal solutions. Dissociation being incomplete in such solutions, any variation of conductivity due to change of ionisation with temperature would be included in his temperature coefficients and might entirely vitiate the deductions which I drew. This portion of my former paper must therefore be withdrawn, and I propose to pursue the matter further experimentally.

$$D = 1{\cdot}86 + 3{\cdot}3\,\delta V_s,$$

where δV_s is the change in the solution volume for different dilutions. This formula would also include a non-electrolyte such as sugar, in which δV_s is almost zero. Furthermore, by correcting the concentration for the amount of water abstracted by and combined with the solute, a constant value was obtained for the effective molecular freezing-point depression of KCl solutions down to a concentration of twice decinormal.

The equivalent refractive power of KCl and NaCl solutions was similarly shown to be a linear function of the ionic volume, and, consequently, also of the solution volume.

In the sketch of the course of the present paper we have passed over some matters arising incidentally which may call for mention. But it must be observed that the main purpose kept in view throughout is to show the interpenetration of the theory of ionic sizes with the theories of the various phenomena of solutions, and to test the theory as far as possible in its relation to such phenomena. In this process various side avenues have been opened up, which we have forborne to follow if they carried us too far from the main track.

One incidental matter of importance is the correction of the coefficient of ionisation which is afforded by the theory, according to which the true value of the coefficient of ionisation is

$$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1 + Bh^{-2{\cdot}3}}.$$

The result of this correction is to make the values of α for KCl and NaCl very nearly the same for equimolecular solutions, down to twice decinormal concentration. In confirmation of this it was found that the observed densities of mixtures of normal solutions of KCl and NaCl were correctly given by the "law of mixtures" within very narrow limits.

The conductivities of these mixtures were also determined and a mixture law for the conductivities based upon the consideration of viscosities and ionic sizes was formulated. The agreement thus obtained between observed and calculated values also tends to show that the hypothesis upon which the calculations were made is correct.

The increase in the ionic volumes which takes place with increasing dilution must be nearly proportional to the increasing volume of water combined with the ion. The development of this matter quantitatively, so as to determine the number of molecules of water in combination with the ion under different circumstances, is a matter of great importance, but it cannot be dealt with in this paper. The effect of water combination as a sufficient and possibly the only cause of ionisation is dealt with, to some extent, in the former paper (see the revised version published in the 'Zeitschrift f. Phys. Chem.,' *loc. cit.*) and has also recently been considered by LOWRY ("An Application to Electrolytes of the Hydrate Theory of Solution," 'Trans. Farad. Soc.,' I., 197, 1905).

PART II.—EXPERIMENTAL DETERMINATIONS.

(*a*) *Density and Viscosity of* NaCl *Solutions at* 18° C.—The material used for the earlier determinations was purest fused NaCl (obtained from BAIRD and TATLOCK). A stock solution of a strength of 21·673 per cent. was prepared, the density of which at 15° C. was found to be 1·1638. MENDELÉEF ('Principles of Chemistry,' ed. 1905, vol. 1, p. 451) gives for the density of NaCl solutions at 15° C. the formula

$$S_{15} = 9991{\cdot}6+71{\cdot}17P+0{\cdot}214P^2 \qquad \text{(water = 10,000).}$$

This formula gives for 21·673 per cent. the density 1·1635.

A further sample of material was purified by precipitation with HCl, recrystallised and fused (specially prepared by MERCK). A stock solution of 20·000 per cent. was made from this sample, the density of which at 15° C. was 1·1502. MENDELÉEF'S formula gives 1·1501. No substantial difference between these solutions manifested itself, but for any range of values the same solution was used.

The densities were determined in all cases in duplicate, by means of a pair of pyknometers, each having a capacity of about 100 cub. centims. The viscosities were determined for the most part by means of the simpler type of viscosimeter described in the former paper. The results from this instrument are indicated in the diagram by black circles. A few determinations which were made with another instrument are indicated by open circles.

The viscosities were calculated from a differential formula derived from the formula

$$\eta = \rho t\,(A - B/t^2).$$

By differentiating we have

$$\delta\eta = \frac{\eta}{\rho}\,\delta\rho + \rho\left(A + \frac{B}{t^2}\right)\delta t.$$

For water, $\eta_{18} = 0{\cdot}010514$, $\rho_{18} = 0{\cdot}99866$; and for the instrument chiefly used, $A = 0{\cdot}000017703$, $B = 0{\cdot}28294$, with a small correction for variations when the time of flow of water at 18° C. varied from 621 seconds.

These constants were determined by the time of flow of water at various temperatures, as derived from THORPE and RODGERS' determinations ('Phil. Trans.,' A, vol. 185, p. 397, 1894), by means of the formula given in a former paper (BOUSFIELD and LOWRY, 'Roy. Soc. Proc.,' vol. 71, p. 47, 1902), viz. :—

$$\eta_{18} = \eta_t\left[1+0{\cdot}0251\,(t-18)+0{\cdot}000115\,(t-18)^2\right].$$

The differential formula becomes on substituting for η, ρ, A, B and t,

$$\delta\eta = 0{\cdot}01053\ \delta\rho + 0{\cdot}000018406\ \delta t.$$

It was found by trial with a series of water values at different temperatures that the differential formula remained sufficiently accurate even when δt amounted to as much as 50 seconds.

The values determined for the less dilute solutions of NaCl are given in the following table :—

TABLE I.—Density and Viscosity of NaCl Solutions at 18° C.

P.	m.	Density.	Viscosity.	Viscosity referred to water as unity.
6	1·068	1·04200	0·01150	1·093
4	0·7024	1·02749	0·01112	1·058
3	0·5232	1·02027	0·01098	1·042
2	0·3463	1·01308	0·01083	1·030
1	0·1720	1·00592	0·01068	1·016
0	0	0·99866	0·010514	1·000

The duplicate density determinations in no case differed by more than a unit in the fifth place of decimals. The air corrections were determined from observation of barometer pressure and laboratory temperature, and it is considered that the densities may be taken to be relatively correct within ± 1 in the fifth place of decimals. The viscosity determinations have not the same order of accuracy.

For the purposes of this paper it was a matter of considerable importance to determine the viscosities of more dilute solutions, but this proved to be a matter of the greatest difficulty. Other observers of viscosities have had the same experience, but whether owing to the same cause is not clear.

In the former paper it was pointed out that the constants of the apparatus, as tested by the time of flow of water at 18° C., vary from time to time in an irregular manner. No amount of washing will bring the apparatus to a steady condition. In dealing with very dilute solutions the variations of the water constant are often of the same order of magnitude as the variations due to variation of concentration of the solution. Hence the only safe method of operation is to interpose between the observations of salt solutions observations of water, which, of course, involves a thorough rinsing of the apparatus, which may in itself introduce some change in its condition.

When a series of observations of solutions with interposed observations of water shows no material change in the water constant, it is assumed that the conditions were the same throughout, and that the observations are therefore accordant. But this assumption is not always true. A very large number of observations on dilute

NaCl solutions were made, many of which had to be rejected in whole or in part, on account of variations in the water constant. Particulars of the best and most accordant set of observations on very dilute solutions are given in Table II.*

TABLE II.

P.	m.	Time of flow.	δt.	$\delta\rho$.	η	Viscosity referred to water as unity.
Water	—	619 618·8	—	—	—	—
0·01	0·00174	619·3 619·4 619·4	0·5	0·00007	0·010524	1·0010
Water	—	619·1 619·5	—	—	—	—
0·04	0·00683	620·0 620·2	1·2	0·00029	0·010539	1·0024
0·0915	0·0156	620·6 620·8	1·8	0·00066	0·010554	1·0038
Water	—	619 618·6 619	—	—	—	—
0·131	0·0223	620·7 620·7	1·8	0·00094	0·010557	1·0041
0·335	0·0573	622·4 622·0	3·3	0·00242	0·010601	1·0083
0·60	0·1025	623·5 623·3	4·5	0·00433	0·010643	1·0123
1·00	0·1720	623·8 624·0	5·0	0·00726	0·010683	1·0161
Water	—	619 618·8	—	—	—	—

In this series the mean value for the time of flow of water at 18° at the beginning and end of the observations remains constant at 618·9. At one point there was a variation in the water constant, but it returned afterwards to the same value, and there appears to be no break in the values for the solutions. δt is therefore calculated throughout from the value for water of 618·9. $\delta\rho$ is calculated from the density at 1 per cent. by a linear formula.

---

* As my viscosity determinations for very dilute solutions differ materially from GRÜNEISEN'S, which are given below, I have thought it well to set out fully the data from which my results are calculated, though very little use has been made of data for solutions below 1 per cent. strength in this paper, except for the initial process of correcting α. The effect of the solute in dilute solution upon the water itself, for which accurate measurements of dilute solutions are required, is left over for the time.

The series of observations set out in the two foregoing tables are plotted in Diagram I., and shown by black circles. A series of observations given in a recent paper by GRÜNEISEN ('Wiss. Abhand., Phys. Tech. Reichs.,' 4, 239, 1905), to which fuller reference will later be made, is also plotted. They are indicated by double open circles, and the values are set out below.

TABLE III.—GRÜNEISEN'S Determination of the Viscosity of NaCl Solutions at 18° C.

m.	Viscosity referred to water as unity.
1	1·0858
0·5	1·0410
0·2	1·0167
0·1	1·0086
0·05	1·0046

It will be observed that in the more concentrated solutions there is a fair agreement. But at the dilute end of the curve the present observations show a considerably greater viscosity than GRÜNEISEN'S observations.

It hardly seems possible that the difference can be due to changes in the apparatus constant during the series, as the water constant is the same at the beginning and end. No other series so coherent as the one set out above was obtained, but the following observations, made with another instrument, tend to show that the difference is slightly greater than is indicated by the above series.

TABLE IV.—Other Determinations of Viscosity of Dilute NaCl solutions.

m.	Viscosity referred to water as unity.
0·00085	1·0025
0·0090	1·0050
0·0120	1·0054
0·01563	1·0054
0·0286	1·0070
0·0343	1·0064
0·0491	1·0077

These determinations have only the value of isolated observations, but they are entitled to some weight, and they are indicated on the diagram by small open circles. The curve drawn on the diagram indicates the line of values actually adopted for the purpose of this paper. It was drawn on a larger scale for the very dilute end, and the values adopted for the different concentrations for very dilute solutions were taken from this curve.

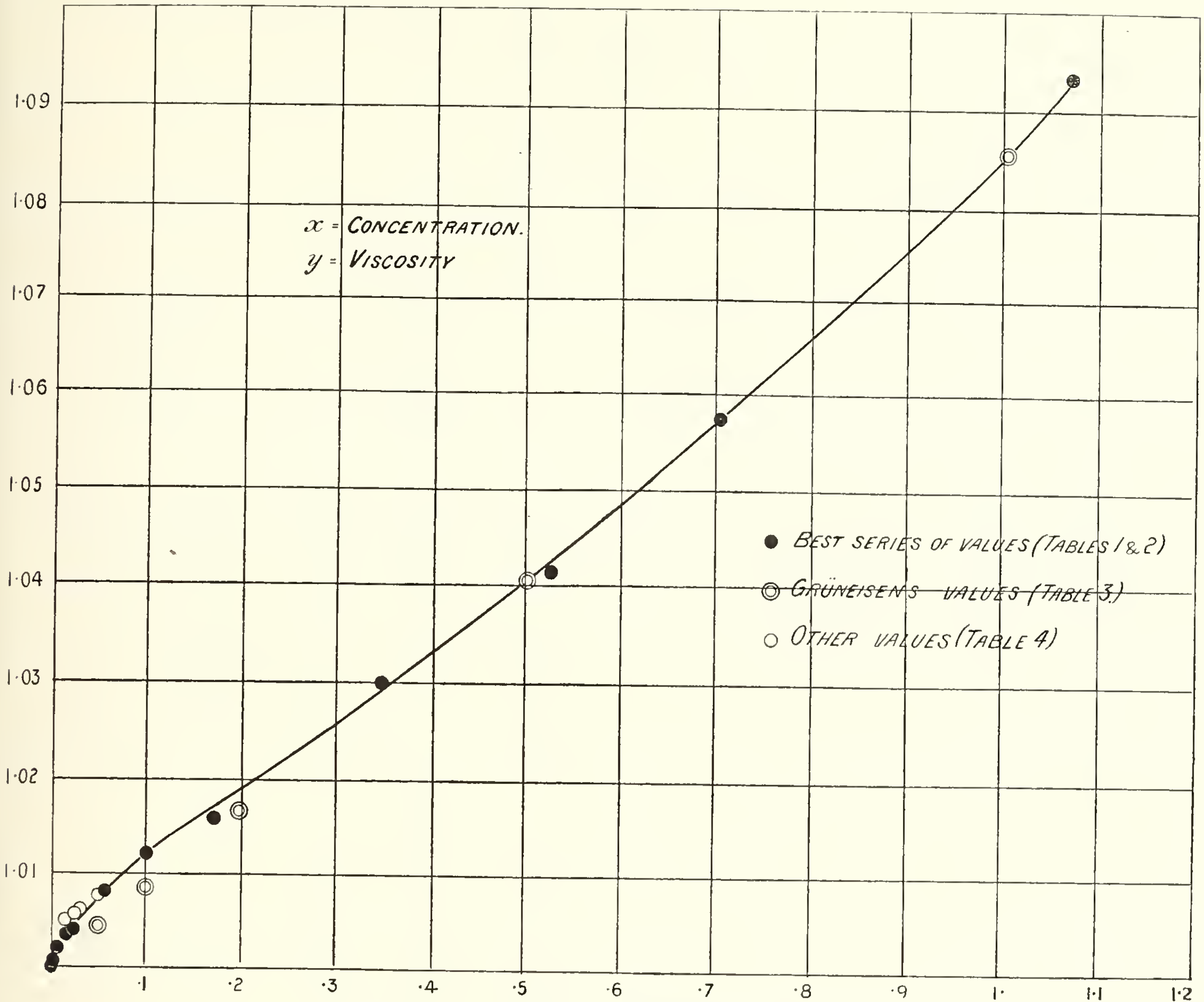

Diagram I. Viscosity of NaCl Solutions at 18° C.

(*b*) *Density, Viscosity and Conductivity of Mixtures of Normal Solutions of* KCl *and* NaCl.—In this series of experiments, stock normal solutions of KCl and NaCl were made up, and the density, viscosity and conductivity of these solutions and of mixtures thereof were determined at 18° C. The mixtures were made by means of 100- and 200-cub. centim. flasks (stamped at the P.T.R.). The densities and viscosities were determined as before described. The conductivities were measured by KOHLRAUSCH's method with wheel bridge and telephone with the special variations described in a former paper (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, p. 286, 1905). The platinum pot containing a glass-shielded electrode was used as the conductivity vessel—resistance capacity = 16·310. The conductivities observed are given in Table X., Part III. (*e*).

The duplicate density measurements corrected for differences of laboratory temperature and barometric pressure were as follows:—

Table V.—Densities at 18° C. of Normal KCl and NaCl Solutions and Mixtures thereof.

Volume KCl.	Volume NaCl.	Density.		Mean density.
		Pyknometer No. 1.	Pyknometer No. 2.	
4	0	1·044955	1·044981	1·04497
3	1	1·043555	1·043530	1·04354
2	2	1·042114	1·042109	1·04211
1	3	1·040668	1·040691	1·04068
0	4	1·039203	1·039217	1·03921

The viscosity measurements were made in two groups, with an interval of three days between. The water constant appears to be steady in each set, but differs by a second for the two sets. The order of accuracy obtained is about ±1 per thousand.

Table VI.—Times of Flow of KCl and NaCl Solutions at 18° C.

Volume KCl.	Volume NaCl.	Water test.	Time of flow.	Mean time.	η.
—	—	Water	622·2 622·2	622·2	—
4	0	—	589·2 589·0	589·1	0·010374
0	4	—	647·6 647·4	647·5	0·011433
2	2	—	616·8 616·6	616·7	0·010884
—	—	Water	622·2	622·2	—
—	—	Water	623·2 622·8 623·2	623·1	—
3	1	—	604·2 604·3	604·2	0·010633
1	3	—	633·5 633·6	633·5	0·011164
—	—	Water	623·4 623·2	623·3	—

The viscosities are calculated from the formula

$$\eta = \rho t\,(\mathrm{A}-\mathrm{B}/t^2),$$

where for the first series

$$\mathrm{A} = 0{\cdot}00001766, \qquad \mathrm{B} = 0{\cdot}2819,$$

and for the second series

$$\mathrm{A} = 0{\cdot}00001763, \qquad \mathrm{B} = 0{\cdot}2811,$$

the constants being corrected for the change of the time of flow of water at 18° in the manner before indicated.

(*c*) *Determination of density of dilute solutions of* KCl *and* NaCl *at* 0° C.—It was necessary for our purpose to determine accurately the solution volumes of dilute solutions of KCl and NaCl at the freezing-point. A pair of pyknometers of large capacity (about 330 cub. centims.) was therefore used for this purpose. The solutions were made up by dilution at 18° C. from normal solutions, and ranged from N/2 to N/32. The pyknometers were packed in ice in a refrigerator for two or three hours in order to secure a correct temperature adjustment. The air corrections for the weighing operation were calculated from the temperature and pressure in the laboratory from time to time. The observed densities are given to the sixth place of decimals, though the sixth place is only of value as fixing the fifth place more accurately.

The "observed" solution volumes are calculated from the densities by means of the formula

$$\mathrm{V}_s = \frac{1}{\rho_0} - \frac{1000}{m\mathrm{E}\rho_0}(\rho-\rho_0),$$

where ρ_0 is the density of water at 0° C., m is the concentration in gram-molecules per litre of solution, E is the equivalent weight of the solute.

In order to obtain expressions for the solution volume in terms of the hydration h, a formula of the same form as is shown to hold for 18° C. was used (*vide post*, Part IV. (*a*)), viz., $\mathrm{V}_s = c - b\gamma$, where $\gamma = (1+\mathrm{B}h^{-2/3})^{-3}$.

For densities at 18° C. we were able to determine B from the conductivities by the method stated in Part III. (*g*). But no sufficiently accurate series of conductivity values at 0° C. was available for determining B in this manner. Hence the value of B was determined by taking trial values of B until, on setting out the resulting values of V_s upon the resulting value of γ, the points ranged approximately in a straight line. A considerable difference in the value of B makes little difference in the values of V_s, or in the limiting value which is obtained by putting $\gamma = 1$.

The value of B was taken as 6 in the case of KCl, and 4 in the case of NaCl, and with these values of B the values of γ were calculated.

The values of h (the number of molecules of water per molecule of solute) are not quite the same for solutions of KCl and NaCl of equal concentration, but this again makes no appreciable difference, and the mean values of h were taken for both. The empirical formulæ thus derived for the solution volumes were

for KCl . . . . $V_s = 0{\cdot}3658 - 0{\cdot}059\,\gamma$,
for NaCl . . . . $V_s = 0{\cdot}3015 - 0{\cdot}089\,\gamma$.

In the following table are set out the observed densities, the "observed" values of the solution volumes (calculated from the observed densities), the values of $h^{-2/3}$ and γ, the solution volumes calculated from the above formulæ and the differences. The values of the solution volumes at infinite dilution (obtained from the above formula by putting $\gamma = 1$) are for KCl 0·3068, for NaCl 0·2125.

TABLE VII.—Densities and Solution Volumes of KCl and NaCl at 0° C.

Concentration.	$h^{-2/3}$.	γ.		Densities.		V_s for KCl.			V_s for NaCl.		
		KCl.	NaCl.	KCl.	NaCl.	Observed.	Calculated.	Difference.	Observed.	Calculated.	Difference.
N/32	0·0068	0·887	0·923	1·001479	1·001305	0·3133	0·3135	− 2	0·2194	0·2194	±
N/16	0·0108	0·820	0·881	1·003061	1·002717	0·3174	0·3174	±	0·2236	0·2231	+ 5
N/8	0·0172	0·745	0·819	1·006203	1·005520	0·3217	0·3218	− 1	0·2285	0·2286	− 1
N/4	0·0274	0·633	0·732	1·012410	1·011058	0·3281	0·3284	− 3	0·2356	0·2363	− 7
N/2	0·0436	0·498	0·617	1·024633	1·021920	0·3364	0·3364	±	0·2465	0·2466	− 1

PART III.—IONIC SIZE IN RELATION TO CONDUCTIVITY.

(*a*) *Theoretical Considerations.*—Some confusion still exists in the use of terms employed in relation to the theory of conductivity, which makes it desirable to state the fundamental equations with precision, and to define the terms used with exactness. It will be convenient to set out together the meanings of the symbols employed.

U = absolute velocity of kation (expressed in centimetres per second) under a potential gradient of 1 volt per centimetre.
V = absolute velocity of anion.
q = quantity of electricity liberated by 1 gramme equivalent of any monad ($q = 98360$ coulombs).
m = concentration of solute in gramme equivalents per litre.
h = hydration (number of molecules of water per molecule of solute).
$u = qU$, $v = qV$, mobilities of the ions.

κ = specific conductivity of solution reckoned in units such that κ^{-1} = resistance in ohms of a centimetre cube of the solution between its opposite sides.

$\lambda = 1000\kappa/m$, the "equivalent conductivity."

Λ = equivalent conductivity at "infinite" dilution.

$l_1 = u_\infty$, $l_2 = v_\infty$, so that $\Lambda = l_1+l_2$.

α = true coefficient of ionisation.

r = radius of an ion.

$R = r_\infty$ = radius of ion at infinite dilution.

η = viscosity in absolute units.

n_2 = Hittorf migration number for anion; $n_1 = 1-n_2$.

Confining ourselves to the case of binary electrolytes composed of monovalent ions, we have

$$\kappa = \frac{am}{1000} \cdot q \cdot (U+V) \quad \text{(1)},$$

$$\lambda = \alpha(u+v) \quad \text{(2)},$$

and at infinite dilution

$$\Lambda = l_1+l_2 \quad \text{(3)}.$$

It is important to note that u and v are the true "mobilities" of the ions, being really proportional to the velocities. The numbers usually tabulated as "mobilities" are αu and αv, whose sum makes up λ. At infinite dilution the distinction ceases to exist, since $\alpha = 1$, but it is important to keep it in mind for less dilute solutions.

According to Stokes' theorem (*vide* former paper), the limiting velocity of a small sphere of radius r in a medium of viscosity η under an applied force P is proportional to $P/r\eta$. Assuming that the ions are spherical and that they are water-coated, so that the friction is always water on water, we should have, if Stokes' theorem is applicable to ionic movements under the electromotive force,

$$r = C/v\eta \quad \text{(4)},$$

where C is a constant for monovalent ions.*

Assuming the validity of the application, the sizes of the ions can be ascertained in absolute units, as is done in Professor Poynting's calculation in reference to the former paper.† But for our present purpose we are concerned with comparative sizes, and are at liberty to simplify the equations by choosing a suitable unit radius. This we do by making C = 1 in equation (4), so that we have always

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* Considerations derived from viscosity measurements of divalent ions render it doubtful whether the same value of C could be applied to them. It may be that divalent ions differ notably from a spherical shape. It is also possible that the H and OH ions, being little, if at all, hydrated, might require a different constant.

† I have set out this calculation in the paper as published in the 'Zeitschrift für Phys. Chem.,' 53, 1905, p. 302.

$$r = 1/v\eta \quad \text{or} \quad 1/r = v\eta \quad \ldots \ldots \quad (5),$$

or, at infinite dilution,

$$R = 1/l.$$

In other words, our unit radius is the radius of an imaginary monovalent water-coated ion which has unit mobility at infinite dilution. All ionic radii will be given in ionic units, as we may shortly term this unit. Moreover, for reasons which will more fully appear hereafter, we shall speak of the ionic radius as the "radion." This will be specially convenient, first, because the radion will be shown to be an important physical quantity, quite apart from our theory that it represents the radius of the hydrated ion; secondly, because, as was shown in the former paper, the value of the ionic radius which we obtain is the *average* value for the whole of the ions, and not the value for any individual ion; and, thirdly, because the conception of the radion is useful, not only in reference to ions, but also to other hydrated molecules, and even to water itself.

Slightly modifying the notation given in the former paper, we have

$$u = \frac{1}{r_1\eta}, \quad v = \frac{1}{r_2\eta}, \quad \lambda = \frac{\alpha}{\eta}\left(\frac{1}{r_1} + \frac{1}{r_2}\right),$$

and writing

$$\frac{R_1}{r_1} = 1+\phi_1, \quad \frac{R_2}{r_2} = 1+\phi_2,$$

where ϕ_1 and ϕ_2 are written as abbreviations for $\phi_1(h)$ and $\phi_2(h)$, so that

$$\frac{1}{r_1} = l_1(1+\phi_1), \quad \frac{1}{r_2} = l_2(1+\phi_2) \quad \ldots \ldots \quad (6),$$

we get for the true value of α

$$\alpha = \frac{\lambda}{\Lambda}\cdot\frac{\eta}{1+\Phi}, \quad \text{where} \quad \Phi = \frac{l_1\phi_1+l_2\phi_2}{\Lambda} \quad \ldots \ldots \quad (7).$$

In the case of KCl it was shown that Φ was of the form $Bh^{-2/3}$. It will be hereafter shown that a function of the same form can be applied with a close approximation to the truth to the case of NaCl. Assuming that ϕ_1 and ϕ_2 are of the same form as Φ, we get

$$B\Lambda = B_1l_1 + B_2l_2 \quad \ldots \ldots \quad (8),$$

when B_1 and B_2 are the constants for the separate ions, and we get for the radions the expressions

$$\frac{1}{r_1} = l_1(1+B_1h^{-2/3}), \quad \frac{1}{r_2} = l_2(1+B_2h^{-2/3}) \quad \ldots \ldots \quad (9).$$

It will be convenient to designate B, B_1, B_2, &c., as the hydration numbers.

By direct determination of the quantities of each kind of ion which pass in opposite directions a given section of a solution in a certain time under the influence of a given current, HITTORF and others have obtained various series of values known as "migration numbers." These are tabulated for the anions, and are often represented by the letter $\mathfrak{n}$, so that

$$\mathfrak{n} = \frac{\text{so-called "mobility" of anion}}{\text{sum of so-called "mobilities" of anion and kation}}.$$

In order to make this fit in with the present nomenclature, it will be convenient to designate the Hittorf number by n_2 and the corresponding number for the kation by n_1. Then we have

$$n_1 = \frac{\alpha u}{\lambda}, \quad n_2 = \frac{\alpha v}{\lambda}, \quad n_1 + n_2 = 1,$$

and for the values of n_1, n_2 at infinite dilution

$$N_1 = l_1/\Lambda, \quad N_2 = l_2/\Lambda.$$

Then, from equations (5), (6), and (7), we get

$$n_1 = \frac{l_1(1+\phi_1)}{\Lambda(1+\Phi)}, \quad n_2 = \frac{l_2(1+\phi_2)}{\Lambda(1+\Phi)},$$

or

$$\frac{n_1}{N_1} = \frac{1+\phi_1}{1+\Phi}, \quad \frac{n_2}{N_2} = \frac{1+\phi_2}{1+\Phi} \quad \text{. . . . . (10).}$$

In the case of KCl and NaCl, equation (8) may be written in the form

$$B = B_1 N_1 + B_2 N_2 \quad \text{. . . . . (11),}$$

which is the relation between the hydration numbers and the migration numbers, and equation (10) gives us

$$n_2 = N_2 + N_2(B_2 - B)(B + h^{2/3})^{-1} \quad \text{. . . . . (12).}$$

There arises thus from our theory a simple linear relation between the series of Hittorf numbers n_2 for an electrolyte and the corresponding series of values of $(B + h^{2/3})^{-1}$. We shall see that this in fact holds, and that equation (12) gives us a ready means for obtaining N_2, the value of the Hittorf numbers at infinite dilution, a quantity of great importance in the theory of electrolytes.

(*b*) *Deduction of Constant for* NaCl.—In the former paper it was shown that in the case of KCl the function Φ was of the form $\Phi = Bh^{-2/3}$, and that the value of B was 3·33. This function was evaluated for KCl upon the hypothesis that the modified Van 't Hoff equation,

$$\log\frac{h}{\alpha} - \tfrac{2}{3}\log\frac{h}{1-\alpha} = C \quad \text{. . . . . (13),}$$

would hold accurately if the coefficient of ionisation were corrected for viscosity and variations of ionic size.* The coefficient of ionisation thus corrected according to our theory takes the form given above in equation (7).

In the case of NaCl it is now found that a similar accord with the law expressed in equation (13) can be obtained with a function of the same form and a value of B = 2·8. This is shown in the following table in which are given corresponding values of m, λ, log h, η, and the other magnitudes involved. The values of η are derived from large scale diagrams of the observed values. For obtaining the values of α there is taken the series of values of λ given by KOHLRAUSCH ('Sitz. der K. Preuss. Akad. der Wiss. zu Berlin,' 1900, p. 1002), $\Lambda = 108·99$. The corrected values of α are calculated by means of equation (7) with the value for $\Phi = 2·8h^{-2/3}$. The column headed C gives the value of the constant C in equation (13) as calculated from these data. The column headed ΔC shows the difference of C from the mean value 0·5049 (which is arrived at without reference to the value for m = 0·0001, for the reasons given in the former paper).

TABLE VIII.

m.	Log h.	λ.	η.†	$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1+\Phi}$.	C.	ΔC.	$\Delta\lambda$.
0·0001	5·74374	108·10	1·0004	0·9918	0·5274	+0·0225	−0·07
0·0002	5·44271	107·82	1·0007	0·9893	0·5052	+0·0003	±
0·0005	5·04477	107·18	1·0011	0·9833	0·5041	−0·0008	±
0·001	4·74375	106·49	1·0014	0·9765	0·5056	+0·0007	−0·01
0·002	4·44271	105·55	1·0018	0·9672	0·5060	+0·0011	−0·01
0·005	4·04475	103·78	1·0029	0·9495	0·5038	−0·0011	+0·02
0·01	3·74368	101·95	1·0041	0·9309	0·5053	+0·0004	−0·01
0·02	3·44259	99·62	1·0055	0·9064	0·5044	−0·0005	+0·03
0·05	3·04444	95·71	1·0087	0·8632	0·5028	−0·0021	+0·09
0·1	2·74304	92·02	1·0126	0·8189	0·5064	+0·0015	−0·08
0·2	2·44131	87·73	1·0184	0·7680	0·5048	−0·0001	+0·01
0·5	2·04105	80·94	1·0408	0·6889	0·5041	−0·0008	+0·05
1·0	1·73592	74·35	1·0857	0·6198	0·5064	+0·0015	−0·12

The column headed $\Delta\lambda$ shows the difference between the observed and calculated value of λ, worked out (as in the former paper) from ΔC. The differences are somewhat more uneven than in the case of KCl, owing partly to the fact that the viscosity correction is larger and probably less accurate, and partly to the fact that the function $Bh^{-2/3}$ does not quite so well represent the correction. But the accurate correspondence of the experimental values with the modified Van 't Hoff law is in this case brought down to normal solutions, within the limits of experimental error; and the divergence is nowhere so great as one per thousand except on the extreme figure. The following table shows the values of α for KCl and NaCl calculated in the ordinary way and the values of α calculated from equation (7) or equation (13).

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* As to this hypothesis, *vide* Appendix, p. 155.

† Referred to water as unity.

It will be seen that whilst the ordinary values of α widely diverge at a concentration of twice decinormal, the corrected values of α are nearly the same. Beyond this point the values diverge.*

TABLE IX.—Values of α.

m.	$\alpha = \frac{\lambda}{\Lambda}$.			$\alpha = \frac{\lambda}{\Lambda} \cdot \frac{\eta}{1+\Phi}$.		
	KCl.	NaCl.	Difference.	KCl.	NaCl.	Difference.
0·0001	0·9921	0·9918	3	0·9916	0·9981	−2
0·0002	0·9898	0·9893	5	0·9890	0·9893	−3
0·0005	0·9847	0·9834	13	0·9833	0·9833	±
0·001	0·9788	0·9771	17	0·9765	0·9765	±
0·002	0·9709	0·9684	25	0·9673	0·9672	+1
0·005	0·9563	0·9522	41	0·9499	0·9495	+4
0·01	0·9411	0·9354	57	0·9311	0·9309	+2
0·02	0·9221	0·9140	81	0·9065	0·9064	+1
0·05	0·8897	0·8782	115	0·8622	0·8632	−10
0·1	0·8611	0·8424	187	0·8194	0·8189	+5
0·2	0·8298	0·8049	249	0·7687	0·7680	+7

A greater divergence in more concentrated solutions is to be expected, and it is important to point out the reason therefor.

(c) *Distinction between Autolytes and Heterolytes.*—In a recent paper (BOUSFIELD and LOWRY, 'Phil. Trans.,' A, vol. 204, p. 256, 1905) attention was drawn to the difference between autolytic and heterolytic conductivity,† and it was shown that an electrolyte, such as sodium hydroxide, which was a good conductor in the melted state, showed clear indications of autolytic conductivity in the more concentrated solutions. It may be supposed that, as in dilute solution, water combination is the effective force producing ionisation, so in the melted state self-ionisation (resulting in autolytic conduction) is produced by the combination of the ions with molecules of the melted salt. In concentrated solution, this action probably still persists, and though we have mainly heterolytic ionisation produced by combination of ions with the solvent, we may have also some autolytic ionisation produced by combination of the ions with molecules of the solute.‡ KCl and NaCl belong to the class of autolytes, and if we took a concentrated solution of either salt at a suitable pressure and a temperature above the melting-point of the salt, and were gradually to drive off the water, we should come gradually to a condition of things in which the conduction was entirely autolytic. Hence we cannot expect the near equality of ionisation which we find in the case of KCl and NaCl at the dilute end of the range to persist at the concentrated end where the idiosyncrasies of self-ionisation may produce a marked effect.

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* Since this paper was communicated, I have made an examination of a group of nine salts with reference to this matter, and have come to the conclusion that no stress should be laid upon the near approach to equality of the values of α for KCl and NaCl. If water combination be the efficient cause of ionisation, one would expect that the great differences in the amount of water combination with different salts would lead to corresponding differences in the values of α. This turns out to be probably the case.

† These words were adopted by Dr. LOWRY and myself at the suggestion of Professor ARMSTRONG, to indicate the phenomena to which attention was called.

‡ This theory has been recently developed in a paper by Dr. LOWRY, 'Trans. Faraday Society,' vol. 1, 1905, p. 197, "An Application to Electrolytes of the Hydrate Theory of Solutions."

(*d*) *Mixtures of* KCl *and* NaCl *Normal Solutions.*—If two solutions have the same ionisation, there should be no change of molecular aggregation upon mixture, since, according to our theory, change of ionisation and change of ionic hydration are necessarily concomitant. Density measurements afford a very sensitive test of changes of molecular aggregation, and the results in this instance show that the change of aggregation upon mixing normal KCl and NaCl solutions in various proportions is very small.

The question of the conductivities of such mixtures has a bearing upon the validity of our main hypothesis. If the conductivities of such mixtures are calculated according to the so-called "law of mixtures," they all come out about 0·0003 too high; but calculated as below they come within 0·0001 of the correct values. The residual difference, both with the densities and the conductivities, may be due to the slight difference in ionisation in normal solutions which we attribute mainly to a difference in autolytic ionisation.

According to our hypothesis we have, for the conductivity of the solutions of KCl and NaCl respectively,

$$\kappa_1 = \frac{m\alpha}{1000} \cdot \frac{1}{\eta_1 r_1}, \quad \kappa_2 = \frac{m\alpha}{1000} \cdot \frac{1}{\eta_2 r_2},$$

where $\frac{1}{r}$ stands for the sum of the reciprocals of the radions in each case.

If we mix a volume V_1 of the KCl solution with a volume V_2 of the NaCl solution, and there is no contraction, we have for the concentrations of KCl and NaCl, respectively, in the mixture

$$m_1 = \frac{mV_1}{V_1+V_2}, \quad m_2 = \frac{mV_2}{V_1+V_2}.$$

Hence, if η be the viscosity of the mixture, we get for the portions of the conductivity of the mixture due to the KCl and NaCl respectively, assuming the coefficients of ionisation to be equal,

$$\frac{\alpha}{1000} \cdot \frac{mV_1}{V_1+V_2} \cdot \frac{1}{\eta r_1} \quad \text{and} \quad \frac{\alpha}{1000} \cdot \frac{mV_2}{V_1+V_2} \cdot \frac{1}{\eta r_2}$$

or

$$\frac{V_1}{V_1+V_2} \cdot \frac{\kappa_1 \eta_1}{\eta} \quad \text{and} \quad \frac{V_2}{V_1+V_2} \cdot \frac{\kappa_2 \eta_2}{\eta}$$

and the sum of these portions gives the combined conductivity

$$\kappa = \frac{\kappa_1\eta_1 V_1 + \kappa_2\eta_2 V_2}{\eta\,(V_1+V_2)}.$$

This, then, should be the true formula for the conductivity of mixtures of equal ionisation.

The formula for calculating the densities of the mixture is, of course, simply

$$\rho = \frac{\rho_1 V_1 + \rho_2 V_2}{V_1+V_2}.$$

In the following table are set out the observed values of the viscosities, densities, and conductivities, together with the calculated values for the densities and conductivities according to the above mixture formulæ. The calculated values for the viscosities of the mixtures are dealt with elsewhere.

Table X.—Mixtures of Normal KCl and NaCl Solutions.

V_1 (KCl).	V_2 (NaCl).	Viscosity observed.	Density.		Difference.	Conductivity.		Difference.
			Observed.	Calculated.		Observed.	Calculated.	
4	0	0·01037	1·04497	—	—	0·0983	—	—
3	1	0·01063	1·04354	1·04353	+1	0·0920	0·0919	+1
2	2	0·01088	1·04211	1·04209	+2	0·0860	0·0859	+1
1	3	0·01116	1·04068	1·04065	+3	0·0800	0·0799	+1
0	4	0·01143	1·03921	—	—	0·0743	—	—

(*e*) *Hittorf Numbers a Function of the Radions.*—From equations (10) and (6) we see that, according to our theory,

$$\frac{n_1}{n_2} = \frac{l_1(1+\phi_1)}{l_2(1+\phi_2)} = \frac{r_2}{r_1},$$

and therefore, since $n_1+n_2 = 1$, we have

$$\frac{1}{n_2} = 1 + \frac{r_2}{r_1}.$$

Hence the reciprocal of the Hittorf number should be a linear function of the ratio of the radions, and the radions for the ions of a given solute are inversely proportional to the migration numbers of the ions.*

The most useful way of testing this relation for KCl and NaCl, since it gives us certain important results and verifies the result predicted by our theory in a form independent of any hypothesis, is to take the relation in the form shown in equation (12), viz.,

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* This simple relation leads to a different method of arriving at the radions from that which is followed in this paper, but it cannot be developed here.

$$n_2 = N_2+N_2(B_2-B)(B+h^{2/3})^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12),$$

which gives n_2 as a linear function of $(B+h^{2/3})^{-1}$, and to set out the values of n_2 as ordinates upon the values of $(B+h^{2/3})^{-1}$ as abscissæ. This is done in Diagrams II. and III. In the following tables are set out the values of the Hittorf numbers

TABLE XI.—Hittorf Numbers for KCl, calculated from the Radions. B = 3·33.

m.	$h^{2/3}$.	$(B+h^{2/3})^{-1}$.	n_2.		Difference.
			Observed.	Calculated.	
0·01	313·2	0·0031	0·506	0·506	±
0·02	197·2	0·0050	0·507	$0·506_3$	+0·7
0·05	107·0	0·0090	0·507	0·507	±
0·1	67·4	0·0141	0·508	0·508	±
0·2	42·4	0·0219	0·509	0·509	±
0·5	23·0	0·0380	0·513	0·512	+1
1·0	14·4	0·0565	0·514	0·515	−1

TABLE XII.—Hittorf Numbers for NaCl, calculated from the Radions. B = 2·8.

m.	$h^{2/3}$.	$(B+h^{2/3})^{-1}$.	n_2.		Difference.
			Observed.	Calculated.	
0·05	107·1	0·0091	0·614	0·614	±
0·1	67·4	0·0142	0·617	0·616	+1
0·2	42·4	0·0221	0·620	0·620	±
0·5	23·0	0·0387	0·626	0·627	−1
1·0	14·4	0·0581	0·637	0·636	+1

according to KOHLRAUSCH ('Leitvermögen der Elektrolyte,' Ed. 1898, p. 201). There are also set out the values of $h^{2/3}$ calculated from the values of m given by KOHLRAUSCH, and the values of $(B+h^{2/3})^{-1}$, taking, for KCl, B = 3·33 and, for NaCl, B = 2·8. There are also given the values of the Hittorf numbers calculated from the expressions

for KCl . . . . $n_2 = 0·5055+0·16\ (B+h^{2/3})^{-1}$,

and for NaCl . . . . . $n_2 = 0·610+0·45\ (B+h^{2/3})^{-1}$.

It will be seen that the agreement between observed and calculated values is very close. This linear relation is quite independent of the theory, but predicted by it, and therefore affords strong support to our hypothesis.

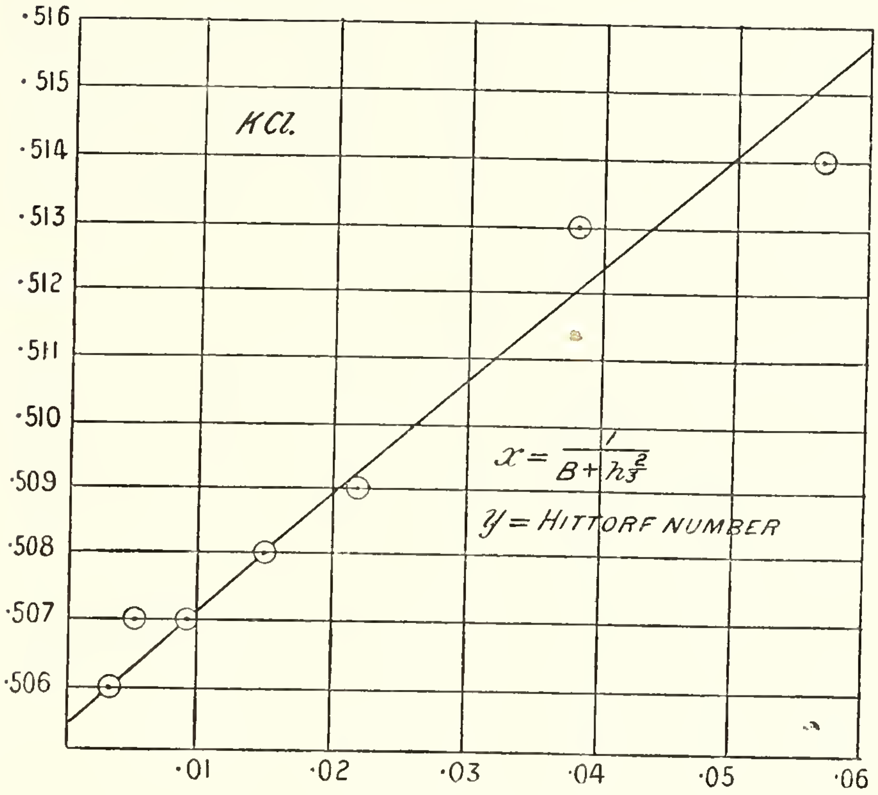

Diagram II.

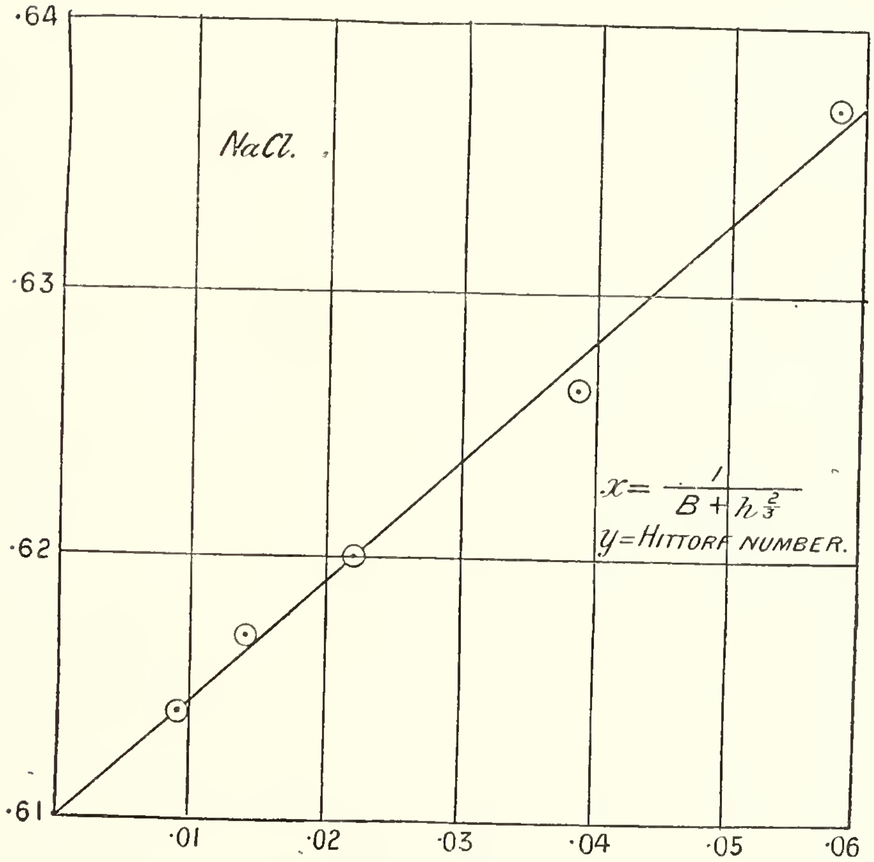

Diagram III.

The value of these equations considered merely as empirical extrapolation formulæ, quite apart from the theory on which they are based, is clear. Putting $h = \infty$, they give us for the values of the Hittorf numbers at infinite dilution the figures 0·5055 and 0·610 respectively, and these are undoubtedly the numbers which must be obtained by extrapolation from the data given by KOHLRAUSCH. But in KOHLRAUSCH'S 1900 paper (*loc. cit.*) he states, without giving further data, that he takes the value of the migration number for KCl as 0·503.

This paper is still the standard paper for the most accurate values of the conductivities of binary electrolytes with monovalent ions. The great accuracy of the values of λ is shown by their correspondence both with KOHLRAUSCH'S empirical formula and with the formula given in this paper—the modified Van 't Hoff law with the corrected coefficient of ionisation. KOHLRAUSCH gives the values of the separate mobilities at infinite dilution as

$$\text{K},\ l = 64{\cdot}67, \quad \text{Na},\ l = 43{\cdot}55, \quad \text{Cl},\ l = 65{\cdot}44,$$

and the values of Λ at infinite dilution as

$$\text{KCl},\ \Lambda = 130{\cdot}10, \quad \text{NaCl},\ \Lambda = 108{\cdot}99.$$

The Hittorf numbers which correspond to these mobilities should be

$$n_2 = \tfrac{65 \cdot 44}{130 \cdot 1} = 0{\cdot}5030 \quad \text{and} \quad \tfrac{65 \cdot 44}{108 \cdot 99} = 0{\cdot}6006.$$

Both of these diverge seriously from the actual values obtained by extrapolation from the data formerly given by KOHLRAUSCH, especially the number for NaCl, which is 0·6004 as against 0·610. It might be well to reconsider the values of the mobilities of the separate ions, in the light of the above given extrapolation formulæ, unless it turns out that KOHLRAUSCH had more accurate but unpublished data in his possession in 1900, since these numbers are of such fundamental importance in the theory of conductivities.

(*f*) *Deduction of Hydration Numbers and Values of Radions and Ionic Volumes.*—It remains now to deduce the hydration numbers for our present purpose.

Comparing the expressions for n_2 above given with equation (12) above set out, the KCl equation gives us for the Cl ion the value $B_2 = 3{\cdot}65$, and the NaCl equation gives us for the Cl ion the value $B_2 = 3{\cdot}54$. This is on the hypothesis that the values of the Hittorf numbers at infinite dilution are 0·5055 and 0·610 respectively. We shall assume, however, that KOHLRAUSCH has data at his disposal which justify his taking the figure for KCl at 0·503 instead of 0·505, which makes the velocities of the K and Cl ions more nearly equal, and we shall provisionally fix the hydration number for Cl at the value 3·5. We then deduce the values for the K and Na ions from the equation

$$B\Lambda = B_1 l_1 + B_2 l_2,$$

and thus get for the values for the K and Na ions,

$$B_{\mathrm{K}} = 3{\cdot}16, \quad B_{\mathrm{Na}} = 1{\cdot}75.$$

The complete series of hydration numbers is then as follows* :—

$$B_{\mathrm{KCl}} = 3{\cdot}33, \quad B_{\mathrm{NaCl}} = 2{\cdot}8, \quad B_{\mathrm{Cl}} = 3{\cdot}5, \quad B_{\mathrm{K}} = 3{\cdot}16, \quad B_{\mathrm{Na}} = 1{\cdot}75.$$

With the aid of the numbers for the separate ions the radions are calculated from the expression

$$r = l^{-1}\,(1+Bh^{-2/3})^{-1},$$

taking the values for l given by KOHLRAUSCH in his 1900 paper and above set out. The values so obtained are set out in the following tables :—

TABLE XIII.—Values of Radions and Ionic Volumes in KCl Solutions.

P.	$\frac{2}{3}\log h$.	r_{K}.	r_{Cl}.	$r_{\mathrm{K}}^3 \times 10^6$.	$r_{\mathrm{Cl}}^3 \times 10^6$.	I_v.
0	∞	0·01546	0·01528	3·692	3·569	7·261
1	1·7418	0·01463	0·01437	3·128	2·968	6·096
2	1·5382	0·01417	0·01387	2·843	2·671	5·514
3	1·4178	0·01380	0·01348	2·627	2·448	5·075
4	1·3315	0·01348	0·01314	2·448	2·268	4·716
6	1·2081	0·01293	0·01256	2·163	1·981	4·144
Normal	1·1542	0·01266	0·01227	2·029	1·852	3·881

TABLE XIV.—Values of Radions and Ionic Volumes in NaCl Solutions.

P.	$\frac{2}{3}\log h$.	r_{Na}.	r_{Cl}.	$r_{\mathrm{Na}}^3 \times 10^6$.	$r_{\mathrm{Cl}}^3 \times 10^6$.	I_v.
0	∞	0·02296	0·01528	12·107	3·569	15·676
1	1·6714	0·02214	0·01422	10·848	2·876	13·724
2	1·4678	0·02167	0·01365	10·177	2·545	12·722
3	1·3474	0·02129	0·01321	9·648	2·303	11·951
4	1·2611	0·02095	0·01282	9·198	2·137	11·335
Normal	1·1573	0·02047	0·01229	8·578	1·852	10·430
6	1·1377	0·02041	0·01218	8·506	1·806	10·312

In the above tables the values of the radions are given in ionic units as before defined. Expressed in the same unit the volume of an ion would be $\frac{4}{3}\pi r^3$. But we shall save trouble, with a gain of convenience, if we take the volume of the ions as $r^3 \times 10^6$. Our unit of ionic volume is therefore the volume of an ion whose radius measured in ionic units is 0·01. The volumes of the ions so calculated are also set out in the tables, together with the total volume of the pair of ions, which is indicated by the letter I_v, and is the sum of the volumes of the two ions.

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* These numbers can only be regarded as approximately fixed. The existence of the discrepancies above indicated in the values of the HITTORF numbers introduces considerable uncertainty. This, however, is not of much consequence in the consideration of dilute solutions, since the magnitude of the radion is primarily fixed by the mobility at infinite dilution, and the hydration number affects only the rate of change of magnitude with dilution, which is small.

The above are the figures which will most frequently be required. Where the values for other concentrations are wanted they can be calculated in the manner above indicated. It will be noticed that the volume of the sodium ion greatly exceeds that of either the K or Cl ion, indicating that the sodium ion is combined with about four times as much water as either of the other two ions.

Part IV.—Ionic Size in Relation to Density.

(*a*) *Solution Volume a Linear Function of Ionic Volume.*—As explained in the former paper, the solution volume derived from density observations is a measure of the amount of contraction which takes place on solution, and therefore a measure of the amount of water entering into combination with the solute. The ionic volumes at different dilutions should be nearly proportional to the amounts of water in combination with the ions, if the volume of water is large compared with the volume of the ionic nucleus. Hence, if our theory is correct, we ought to find the solution volume approximately a linear function of the ionic volume of the pairs of ions in dilute solutions.

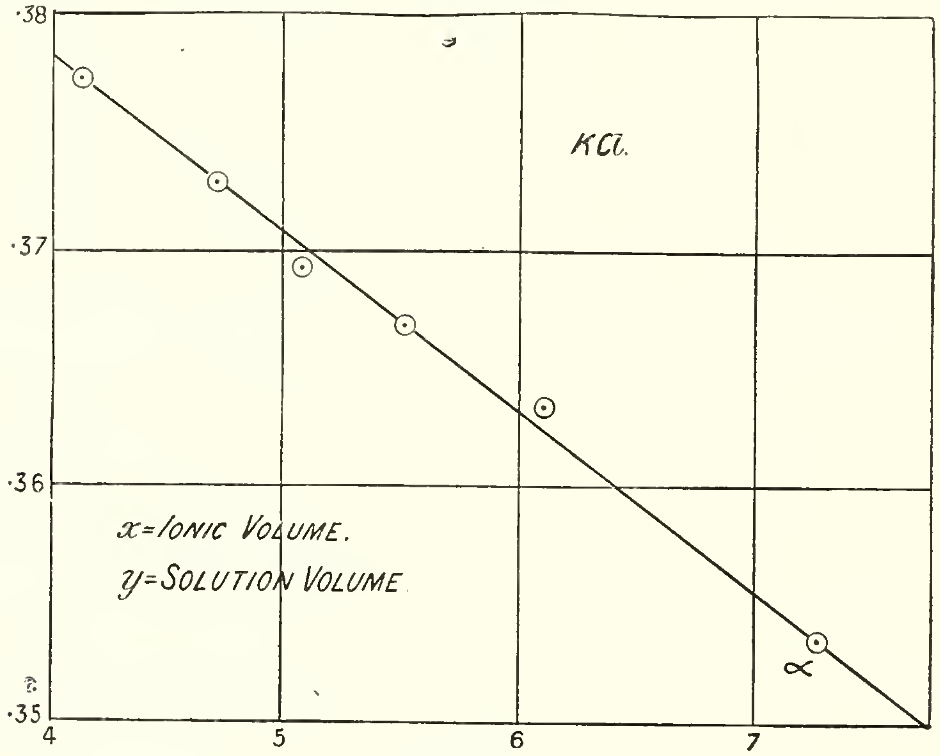

Diagram IV.

In the following tables are set out the solution volumes for KCl and NaCl solutions from 0 to 6 per cent., together with the ionic volumes taken from Tables XIII. and XIV. The solution volumes are calculated from the densities by means of the formula

$$V_s = \frac{1}{\rho_0} - \frac{100}{P}\left(\frac{1}{\rho} - \frac{1}{\rho_0}\right),$$

where ρ is the density of the solution at 18° C. and ρ_0 the density of water. The KCl densities used are given in the former paper. The NaCl densities used are those tabulated in Table I.

In diagrams IV. and V. the solution volumes are plotted as ordinates upon the ionic volumes as abscissæ. They give the following linear relations, from which the calculated values of V_s given in the tables are derived* :—

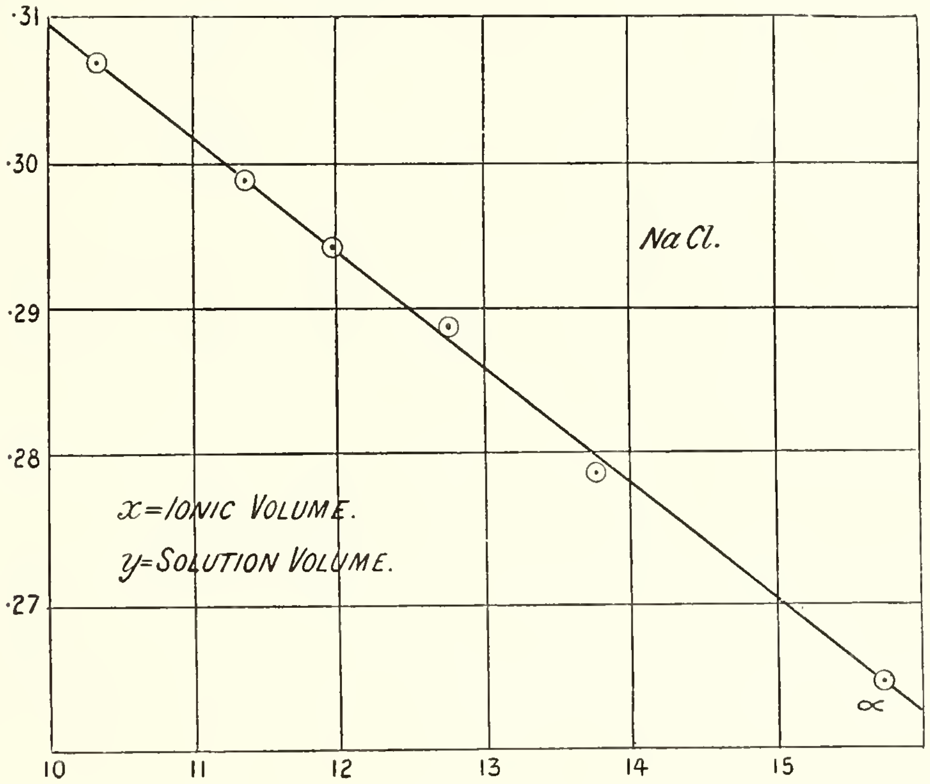

Diagram V.

For KCl . . . . . . $V_s = 0{\cdot}408 - 0{\cdot}0075 I_v$,

for NaCl . . . . . . $V_s = 0{\cdot}390 - 0{\cdot}0080 I_v$.

Table XV.—Ionic and Solution Volumes for KCl.

P.	I_v.	V_s (from density).	V_s calculated.	Difference.
6	4·144	0·377	0·377	±
4	4·716	0·373	0·373	±
3	5·075	0·369	0·370	−1
2	5·514	0·367	0·367	±
1	6·096	0·363	0·362	+1
0	7·261	—	0·354	—

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* In the former paper the hydration numbers B_1 and B_2 for K and Cl were taken as equal. The revised figures for KCl are therefore here given.

TABLE XVI.—Ionic and Solution Volumes for NaCl.

P.	I_v.	V_s (from density).	V_s calculated.	Difference.
6	10·31	0·307	0·307	±
4	11·34	0·299	0·299	±
3	11·95	0·294	0·294	±
2	12·72	0·289	0·288	+1
1	13·72	0·279	0·280	−1
0	15·68	—	0·265	—

(*b*) *Density a Function of Radions.*—As in the former paper, we may now proceed to deduce a rational density formula for KCl and NaCl from the expressions for the solution volumes.

The densities are given by the expression

$$\frac{1}{\rho} = \frac{1}{\rho_0} - \frac{P}{100}\left(\frac{1}{\rho} - V_s\right).$$

As V_s has been expressed in each case as a function of the radions, we now have the densities expressed simply as a function of the radions. The agreement between observed values and values calculated from the radions is shown in the following tables:—

TABLE XVII.—Density of KCl, calculated from Radions.

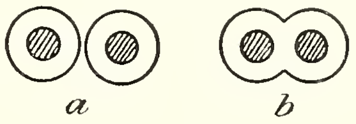
P.	ρ observed	ρ calculated.	Difference.
6	1·03745	1·03747	−2
4	1·02437	1·02439	−2
3	1·01749	1·01792	+2
2	1·01148	1·01148	±
1	1·00507	1·00507	±

TABLE XVIII.—Density of NaCl, calculated from Radions.

P.	ρ observed.	ρ calculated.	Difference.
6	1·04201	1·04199	+2
4	1·02750	1·02748	+2
3	1·02027	1·02026	+2
2	1·01308	1·01309	−1
1	1·00592	1·00591	+1

In both cases the formulæ hold with great accuracy.

The above results are calculated as if the solution were fully ionised, the ionic volume for a pair of ions being taken as the sum of the volumes of the ions. Now, ionisation could only be complete for very dilute solutions, but we find that our formulæ hold without sensible loss of accuracy nearly up to normal solutions for which the coefficient of ionisation is less than 0·7. This is a matter of some practical importance hereafter, as it is an indication that we can take the ionic volume of the *un-ionised* molecules as being approximately equal to the sum of the volumes of pairs of ions with radii given by the formulæ obtained for the separate ions. This means that if we consider a pair of ions just after ionisation to be represented by *a* in the figure, we may consider a pair of ions just before ionisation to be represented by *b*. Hence, while a consideration of conductivities and mobilities only gave us a clue to the size of the ions themselves, the density formula indicates that in solutions of moderate dilution the volumes of the un-ionised molecules may be taken to follow approximately the same law.



Part V.—Ionic Size in Relation to Viscosity.

(*a*) *Viscosity a Function of the Radions.*—We discuss further on the general relation between the viscosity of a fluid and the sizes of the molecules of which it is composed. For the moment, it will suffice to say that it seems, *à priori*, probable that the *change of viscosity* caused by the introduction of foreign molecules

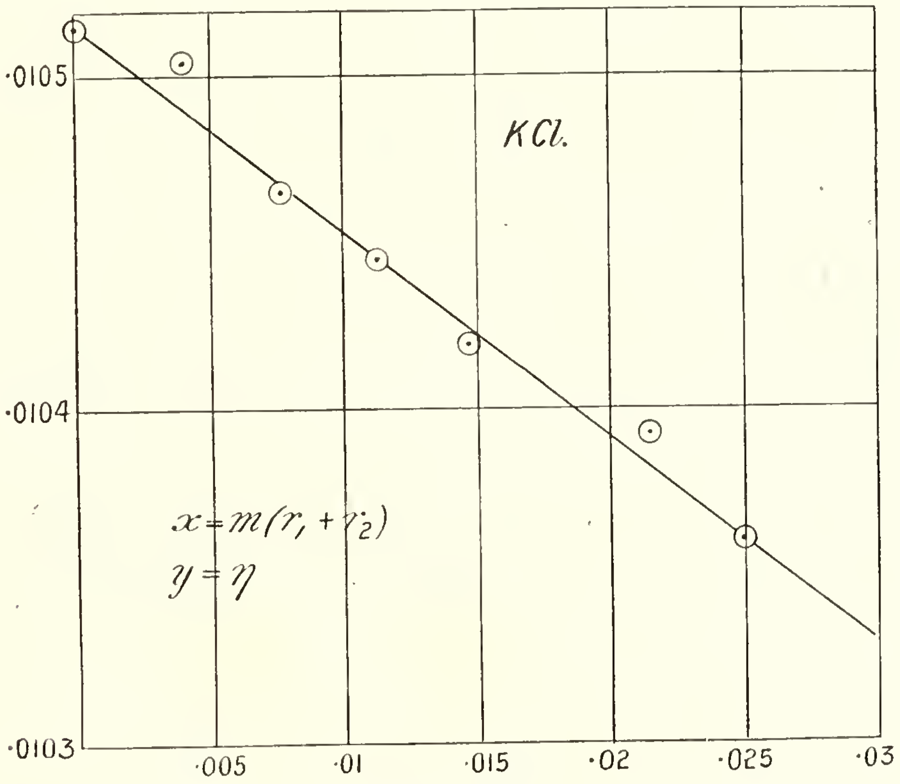


Diagram VI.

into water would depend upon the number and size of the molecules so introduced. According to the theory postulated, an ion is a compound molecule consisting of the ionic nucleus with its envelope of water molecules, as are also the un-ionised molecules of the solute. Hence, if the theory be true, we should expect to find a close relation between the viscosity of the solution and the number and size of these aggregates. The number of molecules depends upon the concentration m, and the *size* upon the radions; the product $m(r_1+r_2)$ should therefore be a measure of the joint effect of the introduced ions upon the viscosity in dilute solutions.

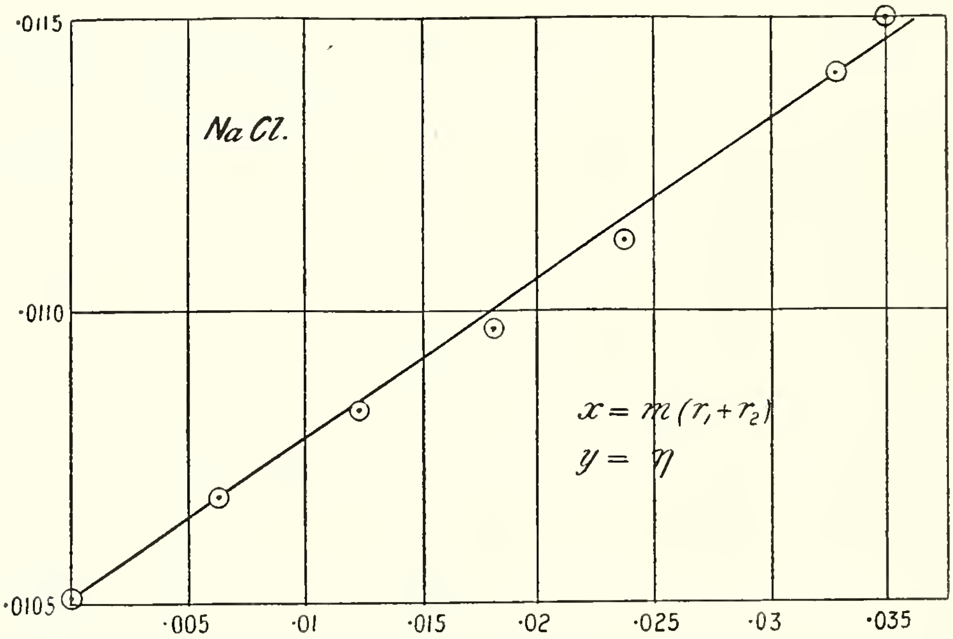


Diagram VII.

In the following tables are set out the concentrations, the sums of the radions, the products $m(r_1+r_2)$ and the observed and calculated viscosities for KCl and NaCl. In Diagrams VI. and VII. the viscosities are set out as ordinates upon the products $m(r_1+r_2)$ as abscissæ. It will be seen that the viscosity is approximately a linear function of $m(r_1+r_2)$, the expressions being

$$\text{for KCl} \quad . \quad . \quad . \quad \eta = 0{\cdot}010514 - 0{\cdot}00578\, m(r_1+r_2) \quad . \quad . \quad . \quad (14),$$

$$\text{for NaCl} \quad . \quad . \quad . \quad \eta = 0{\cdot}010514 + 0{\cdot}0272\, m(r_1+r_2) \quad . \quad . \quad . \quad . \quad (15).$$

TABLE XIX.*—Viscosity of KCl Solutions, calculated from KCl Radions.

P.	m.	r_1+r_2.	$m(r_1+r_2)$.	η Observed.	η Calculated.	Difference.
0	0·0	0·03074	0·0	0·010514	0·010514	±
1	0·1347	0·02900	0·003906	0·010504	0·010491	+13
2	0·2712	0·02804	0·007605	0·010465	0·010470	−5
3	0·4094	0·02728	0·011168	0·010445	0·010450	−5
4	0·5493	0·02662	0·014623	0·010419	0·010430	−11
6	0·8344	0·02549	0·021269	0·010393	0·010391	+2
Normal	1·000	0·02493	0·02493	0·010374	0·010374	±

TABLE XX.*—Viscosity of NaCl Solutions, calculated from NaCl Radions.

P.	m.	r_1+r_2.	$m(r_1+r_2)$.	η Observed.	η Calculated.	Difference.
0	0·0	0·03824	0·0	0·010514	0·010514	±
1	0·1720	0·03636	0·00625	0·01068	0·01068	±
2	0·3463	0·03532	0·01223	0·01083	0·01085	−2
3	0·5232	0·03450	0·01805	0·01097	0·01100	−3
4	0·7024	0·03377	0·02372	0·01112	0·01116	−4
Normal	1·000	0·03276	0·03276	0·01143	0·01141	+2
6	1·068	0·03259	0·03480	0·01150	0·01146	+4

Moreover, if our reasoning is correct, the viscosities of mixtures of normal solutions of KCl and NaCl ought to be given by the formula (derived from the two preceding)

$$\eta = 0{\cdot}010514 - 0{\cdot}00578\alpha\, m\,(r_{\mathrm{K}} + r_{\mathrm{Cl}}) + 0{\cdot}0272\,(1-\alpha)\, m\,(r_{\mathrm{Na}} + r_{\mathrm{Cl}}) \quad . \quad . \quad . \quad (16),$$

where α represents the fraction of the volume of the mixture which consists of normal KCl, and $(1-\alpha)$ the fraction which consists of normal NaCl. m in this case is unity, since we are dealing with mixtures of normal solutions, and taking the sums of the radions at normal dilution from the preceding tables, the expression becomes

$$\eta = 0{\cdot}010514 - 0{\cdot}000144\alpha + 0{\cdot}000892\,(1-\alpha).$$

In the following table the observed values of the viscosity of mixtures of normal NaCl and KCl solutions are taken from Table VI. *ante*, and the calculated values are those given by the above equation.

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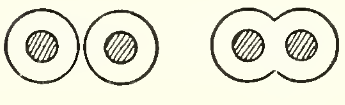
* The observed values of η for KCl from 0 to 6 per cent. are taken from the former paper. The values for the normal solutions of KCl and NaCl are taken from Table VI. Being taken from a different series of observations, they do not range well with the percentage series, but the discrepancy, for our present purpose, is not material.

TABLE XXI.—Viscosity of Mixtures of Normal KCl and NaCl Solutions, calculated from the Radions.

α	η Observed.	η Calculated.	Difference.
1	0·01037	0·01037	±
0·75	0·01063	0·01063	±
0·5	0·01088	0·01089	−1
0·25	0·01116	0·01115	+1
0·0	0·01143	0·01141	+2

The agreement between observed and calculated values in Tables XIX., XX., and XXI., is sufficient to show that the *chief element* which determines the viscosity of the solutions is the product $m(r_1+r_2)$. But the expressions (14), (15), and (16), are not put forward as true viscosity formulæ for KCl and NaCl. They are only intended to show that the viscosity of the solutions is *mainly dependent on the size of the radions.* The results tend strongly to confirm the fundamental hypothesis as to the character of the magnitudes which we have called "radions," and which we derived from the conductivities by the application of the Stokes theorem and the Van 't Hoff law.

It is surprising that the agreement with the observed values in Tables XIX. and XX. should be so close when we consider that at normal concentration the ionisation is less than 0·7. This may be explained on our theory in the following way. As indicated by the agreement upon the density formulæ (see Tables XVII. and XVIII.), *there appears to be no break in the hydration law as between ionised and un-ionised molecules.* Thus, if a represents the condition of things when the molecule is just sufficiently hydrated for ionisation, and (b) the condition of things shortly before ionisation, the same functions approximately express the ionic radii before and after ionisation. A little consideration will show that the expression $m(r_1+r_2)$ *takes the radion of the un-ionised molecule as* r_1+r_2. For if α be the ionisation, this would give us for the separate ions the products $\alpha m r_1$ and $\alpha m r_2$, and for the un-ionised molecule the product $(1-\alpha)m(r_1+r_2)$. The sum of the three products is simply $m(r_1+r_2)$. This seems to explain why the linear relation, which might be expected to obtain between $m(r_1+r_2)$ and η for dilute solutions, does in fact approximately persist up to normal solutions.



(b) *References to Previous Theories.*—The results obtained in the last section suggest considerations which may tend to a great simplification of our ideas in reference to the internal friction of fluids. Hitherto, very diverse theories have been advanced in order to account for the *apparent* anomalies in the viscosity of liquids, and various general formulæ have been proposed in order to express the experimental facts. ARRHENIUS proposed a formula of the form $\eta = C^m$ ('Zeit. f. Phys. Chem.,' 1, 285, 1887) to express the viscosity of a solution in terms of the concentration. For a mixture he proposed $\eta = C_1^{m_1}C_2^{m_2}C_3^{m_3}\ldots$ This formula in the case of KCl, where the constants for the two ions could be taken as approximately equal, reduced to the form $\eta = C_1^{m_1}C_2^{2m_2}$. In this form EULER ('Zeit. f. Phys. Chem.,' 25, 536, 1898) further investigated the matter. Neither of these formulæ turned out to be of general validity.

GRÜNEISEN* ('Wiss. Abh. der Phys.-Tech. Reichsanstalt,' 4, 239, 1905) has elaborated a very accurate formula which takes the form

$$\frac{\eta - \eta_0}{m} = A\alpha + B(1-\alpha) + Cm,$$

where α is the coefficient of ionisation. GRÜNEISEN has given the constants A, B, and C for a large number of electrolytes, and the formula brings out the important fact that the equivalent viscosity increment for electrolytes has *a minimum value* at concentrations varying from normal to $\frac{1}{5}$ normal. But GRÜNEISEN'S results stop short of furnishing a theoretical explanation of the facts. He observes (*loc. cit.*, p. 250):—

"That the minimum found with electrolytes should result from experimental errors, I regard as impossible. The only doubt is whether it is peculiar to electrolytes. I held this idea at first, but further experiments are certainly desirable. This suggests the possibility that the phenomenon may be accounted for by the dissociation of the molecules. On this supposition, the increase of the equivalent viscosity increment at greater dilution would be most simply explained by assuming that the *dissociation of the molecule always increases the friction of the solution.*"

Other observers who have theorised on supposed viscosity anomalies have tendered widely differing explanations. ARRHENIUS ('Zeit. f. Phys. Chem.,' 1, 296, 1887), referring to the lowering of viscosity, or so-called "negative friction," which results from the solution of certain substances, such as KCl, suggests that the *lowering of the friction is a result of electrolytic dissociation.* EULER ('Zeit. f. Phys. Chem.,' 25, 541, 1898) suggests that the change of viscosity in a solution consists of two components, first, an increase which is in inverse proportion to the mobilities of the ions, and, secondly, a component depending upon the compression (electrostriction) of the water through the electric charge of the ions. WAGNER ('Zeit. f. Phys. Chem.,' 46, 871, 1903) controverts both these views, and adumbrates the view (based upon mixtures of alcohol, nitro-toluol, and other organic compounds) that the viscosity of a mixture depends upon the viscosity of its components, and that this will account for "negative friction."

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* GRÜNEISEN'S paper came to my notice whilst the present paper was in progress. His results afford strong confirmation to the hypothesis with which this paper is concerned, and a fuller reference is made to them later.

One matter of great importance has been established in relation to viscosity, viz., that it is an "additive" property. This is due, in the first instance, to the work of REYNER ('Zeit. f. Phys. Chem.,' 2, 744, 1888) and WAGNER ('Zeit. f. Phys. Chem.,' 5, 46, 1890), and finally has been placed on a very firm foundation by GRÜNEISEN (*loc. cit.*).

(*c*) *À priori Considerations leading to a General Viscosity Formula.*—The results obtained in section (*a*) appear to point to the simple view that the viscosity of a solution is in the main merely a function of the number and size of its component molecules. We there saw that the *change of viscosity* of a liquid could be approximately expressed in terms of the size and number of the molecules of the solute introduced, both in the case of simple salts and of mixtures. But the viscosity of the solvent itself should be capable of similar expression. According to STOKES' theorem, the resistance to a very small sphere moving in a viscous medium is proportional to its radius. *À priori* this would lead us to the hypothesis that the viscosity of the medium itself would be proportional to r, in the case of a simple homogeneous medium consisting of molecules of radius r. Furthermore, this, in conjunction with the result which appears in section (*a*), suggests the hypothesis that the viscosity of a heterogeneous medium, consisting of molecules of radii r_1, r_2, r_3, ..., in proportions m_1, m_2, m_3, ..., could be expressed as

$$\eta = \frac{C_1 m_1 r_1 + C_2 m_2 r_2 + \ldots}{m_1 + m_2 + \ldots}.$$

In the general case, the different sorts of molecules might have different coefficients of friction, so that the constants C_1, C_2, C_3 would have different values. But, in the case of aqueous solutions, supposing the ions and molecules to be sufficiently hydrated, we should have, both in the case of water molecules and molecules of the solute, the friction of water on water. We will confine ourselves to this case and take the constant as the same for the different molecules, so that our expression would be simply

$$\eta = C\Sigma mr/\Sigma m.$$

This would possibly exclude the case of H and OH ions, which are possibly little, it at all, hydrated. In case of molecules differing much from the spherical form either a special coefficient of friction would have to be assigned to them, or their radion would have to be taken as their largest or some mean dimension.

The numbers m_1, m_2 might be regarded as expressing either the relative numbers of the various molecular species or their relative amounts reckoned by the total volumes occupied by each species in the solution. In some cases it will make no difference which view we adopt, in others it may make a serious difference. It is easier to work with relative volumes, and we find that such a volume relation holds for the changes of viscosity of mixtures of normal KCl and NaCl solutions. We shall therefore adopt this alternative in order to test the hypothesis, bearing in mind, however, that this is merely a tentative selection from the alternatives. Hence, if $\beta_1, \beta_2, \beta_3, \ldots$ represent the total volumes occupied in the solution by each species of molecules, we propose to represent the viscosity of the solution as

$$\eta = \mathrm{C}\Sigma\beta r/\Sigma\beta.$$

In order to simplify matters, we shall always take $\Sigma\beta = 1$, so that $\beta_1, \beta_2, \beta_3, \ldots$ will be the fractions of the total volume of the solution occupied by each species of molecules, and the expression becomes

$$\eta = \mathrm{C}\Sigma\beta r.$$

(*d*) *Extended Conception of the Radion.*—The conception of the radion as the average molecular radius of any set or sets of molecules, basing the average on a volume reckoning, will greatly simplify the hypothesis. We adopted the term "radion" as a convenient contraction for the *radius of the ion*, which we supposed to be an aggregate consisting of the ionic nucleus and water molecules. The expressions which we obtained for the ionic radius in terms of hydration, which were of the form

$$r = r_\infty (1+\mathrm{B}h^{-2/3})^{-1},$$

clearly indicated that the radius so derived must be an *average* radius, since the hydration h is a *continuously* varying magnitude, whilst the actual numbers of molecules must be whole numbers and must vary *per saltum.* We may now generalise the conception of the radion and use the term to indicate the average radius of any group of molecules. Suppose, then, we have a liquid containing a volume β_1 of molecules of radius r_1, a volume β_2 of molecules of radius r_2, and so on, the radion of this liquid, taking the average on a basis of volumes, would be

$$\mathrm{R} = \Sigma\beta r/\Sigma\beta.$$

If we always consider a unit of volume so that $\Sigma\beta = 1$, and therefore $\beta_1, \beta_2, \ldots$ are the fractions of the total volume occupied by each set of molecules, then we have for the radion, or average molecular size, simply $\mathrm{R} = \Sigma\beta r$.

It follows also that if $r_1, r_2, r_3, \ldots$ be the radions of different volume fractions $\beta_1, \beta_2, \beta_3 \ldots$ of the liquid (instead of the radii of the ultimate molecules) the radion of the liquid is still expressed as $\mathrm{R} = \Sigma\beta r$.

(*e*) *The General Viscosity Formula.*—The general viscosity formula for aqueous solutions in which the coefficients of friction between the molecules may be taken as constant throughout, to which we were led by *à priori* considerations, was $\eta = \mathrm{C}\Sigma\beta r$.

The conception of the radion enables us to express this simply as $\eta = \mathrm{CR}$, where R is the radion of the whole solution. Also if the liquid be composed of various composite constituents having radions $r_1, r_2, r_3, \ldots$ for the respective volume fractions $\beta_1, \beta_2, \beta_3, \ldots$, the viscosity of the separate fractions (if they could be separated) would be Cr_1, Cr_2, Cr_3, ..., and the viscosity of the whole $\eta = C\Sigma\beta r = CR$, if R is the radion of the whole, since $R = \Sigma\beta r$.

We have determined the values of the radions for K, Na and Cl ions in Part III. (*g*) of this paper. In extending the conception of the radion to the molecules of the solvent or to other molecules, its magnitude in any particular case must be measured in the same ionic units, and by reference to the scale furnished by the ions whose radions we have determined. Thus we know, upon our theory, the radions of K and Cl ions, which are approximately equal, and we find that the introduction of such ions into water makes, speaking roughly, no change in the viscosity of the water. This tells us at once (if we neglect the small change in the water radion which is probably produced by the solute) that *the radion of water is of about the same magnitude as the radions of the* K *and* Cl *ions.* As a fact, the introduction of these ions slightly diminishes the viscosity of water and hence the radion of the uncombined water in the solution should be somewhat greater than the radions of K and Cl ions.

There is good reason for believing that the introduction of a solute into water somewhat lowers the radion of water, since the process of abstraction of water molecules by the solute breaks up some of the molecular complexes of the uncombined water and therefore lowers the average molecular size of the un-combined water. The investigation of the amount of this lowering is a complex matter, and we shall neglect it, as it does not seriously affect the general character of our results, though it involves a slight loss of accuracy.

The fundamental constant C of our viscosity equation is calculated from the experimental data in reference to water and KCl and NaCl solutions, but it is not necessary to give the details of the process. The justification of the value given and also of the theory involved is to be found in the correspondence between observed and calculated values given later. The value of C determined from the data at 18° C. is $C = 0{\cdot}54$.

No closer adjustment of its value is at present attainable. This value gives the radion for pure water as

$$R = \eta/C = \frac{0{\cdot}010514}{0{\cdot}54} = 0{\cdot}01947.$$

(*f*) *Experimental Verification.*—We now proceed to test the hypothesis by reference to the experimental data before given. Taking first the simple case of mixtures of KCl and NaCl normal solutions, we have here solutions which do not materially change their state of aggregation upon mixing. We can therefore take the radions of the solutions before mixing as being identical with their radions when mixed. The radion of the normal KCl solution is

$$\eta/C = \frac{0{\cdot}010374}{0{\cdot}54} = 0{\cdot}01929.$$

The radion of the NaCl normal solution is

$$\eta/C = \frac{0{\cdot}011433}{0{\cdot}54} = 0{\cdot}02117.$$

In this case the value of C makes no difference to our results. The water radion is not required, as we can take the radion of *the whole of each solution*, before mixing, as the basis of our calculation, thus accounting for the total number of molecules both of solvent and solute. The constant is here introduced as illustrating the procedure in the more complex case. Care must be taken to distinguish between the radion of a salt solution as a whole, and the radion of the salt in solution.

In the following table are set out the observed values of the viscosities for the mixtures, and the values calculated from the equation $\eta = 0{\cdot}54\ \Sigma\beta r$, where β_1, β_2 are the fractions of KCl and NaCl respectively in unit volume of the mixture.

TABLE XXII.—Viscosities of Mixtures of KCl and NaCl Normal Solutions, calculated from their Radions.

β_1.	β_2.	η observed.	η calculated.	Difference.
1	0	0·01037	0·01037	±
0·75	0·25	0·01063	0·01063	±
0·5	0·5	0·01088	0·01090	−2
0·25	0·75	0·01116	0·01117	−1
0	1	0·01143	0·01143	±

Let us now apply the equation to the general case of a salt in solution. Let r be the radion of the uncombined water in the solution (which may be different from the radion of water itself). Let r' be the radion of the hydrated solute (comprising both ions and molecules). Let β be the total fraction of unit volume of the solution which is occupied by the hydrated ions and molecules of the solute. Then $1-\beta$ will be the fraction which is occupied by uncombined water. Then the equation $\eta = \mathrm{C}\Sigma\beta r$ takes the form $\eta/\mathrm{C} = (1-\beta)\,r+\beta r'$, or

$$\eta/\mathrm{C}-r = \beta\,(r'-r) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17).$$

This may be regarded as the fundamental viscosity equation for a simple salt solution. It may be noted that if we take r as the radion for pure water, we have its viscosity $\eta = \mathrm{C}r$, so that for solutions so dilute that the value of the water radion is not sensibly changed by the addition of the solute we may say

$$\delta\eta = \mathrm{C}\beta\,(r'-r),$$

which indicates that if the radion of the solute is less than that of water $\delta\eta$ is negative. This is in fact the case for KCl, the solutions of which have a less viscosity than water. Cases of "negative friction" therefore are readily explicable upon the present hypothesis.

So far the matter is simple, but in applying the above equation in practice we meet with difficulties which are small for very dilute solutions, but increase with the concentration.

In considering what we are to take as the radion of the group of un-ionised molecules, our difficulties begin. But we saw that in our rough viscosity formula for KCl and NaCl no serious error up to 6 per cent. was introduced by taking the radion of the un-ionised molecule as the sum of the radii of the united ions. This would probably give too large a value, which would vitiate our equations at higher concentrations, but, within the range of concentration with which we are dealing, does not introduce a serious error.

The calculation of the *volumes* of the un-ionised molecules presents a further difficulty. The un-ionised molecules must be combined with less water than the pairs of ionised molecules, but a consideration of the density law showed us that we might without serious error up to 6 per cent. reckon the volumes of the molecules as though they were composed of pairs of spheres, the radii of which followed the same law as the ionic radii. We shall therefore continue to reckon the volume in this way, though it may give too much volume to the un-ionised molecule, in a proportion which will increase with increasing concentration.

The total fraction of volume of the solution occupied by any set of ions will be approximately proportional to the number and volume of the individual ions, but not exactly. If r_1, r_2 be the radions of the separate ions of an electrolyte (reckoned in ionic units), we reckoned the separate ionic volumes as $v_1 = r_1^3 \times 10^6$, $v_2 = r_2^3 \times 10^6$, leaving out the multiplier $\frac{4}{3}\pi$ and introducing the multiplier 10^6 for the sake of convenience. We also took the volume of *either a pair of ions or a molecule* as

$$I_v = V_1 + V_2 = (r_1^3 + r_2^3) \times 10^6.$$

In order to calculate the absolute volumes from the ionic volumes, we must introduce a suitable factor γ. The total volume occupied by the hydrated ions and molecules in a litre of solution being approximately proportional to mI_v, let us represent the fraction of a unit of volume of the solution which is occupied by the ions and molecules of the solute by $\gamma m I_v$. γ will be nearly the same for different molecules, but not quite, since molecules of different volumes do not exactly displace proportionate numbers of molecules of the solvent.

If α be the coefficient of ionisation, the volumes occupied by the ions and molecules respectively will then be

$$\alpha\gamma m V_1, \quad \alpha\gamma m V_2, \quad (1-\alpha)\gamma m (V_1 + V_2).$$

Therefore in unit volume of solution the total volume of the hydrated ions and molecules is $\gamma m (V_1 + V_2)$ or $\gamma m I_v$, and the volume of uncombined water is $(1 - \gamma m I_v)$.

Hence, if r is the radion of water, the general equation $\eta = C\Sigma\beta r$ becomes

$$\frac{\eta}{C} = (1 - \gamma m I_v) r + \alpha\gamma m V_1 r_1 + \alpha\gamma m V_2 r_2 + (1-\alpha)\gamma m (V_1 + V_2)(r_1 + r_2),$$

which reduces to

$$\frac{\eta/C-r}{\gamma m(V_1+V_2)} = R-r, \quad \text{where} \quad R = r_1+r_2-\alpha\frac{V_1r_2+V_2r_1}{V_1+V_2}.$$

R is of course (*vide* equation *ante*) the radion of the solute, and the equation, when written in the form

$$\eta/C = r+\gamma m I_v(R-r),$$

is seen to be identical with the general equation (17) before given.

In the following tables are set out the values of R and η, calculated from the above expressions, together with the necessary data for the calculations. The ionic data are taken from Tables XIII. and XIV. The values of α are obtained by setting out the corrected values of α (given in Table IX.) on a large-scale curve and taking off the values for the different values of m. The observed values of the viscosities are the same as in Tables XIX. and XX. The values of γ used for the calculation were 0·032 for KCl and 0·030 for NaCl. These are mean values calculated from the separate sets of figures for the two salts. The value of r, the radion of the uncombined water, is taken as 0·01946 in both cases. The value of C was worked out from these two sets of figures and the mean value 0·54 was obtained, as before mentioned.

Considering the various slight inaccuracies involved in the approximations above detailed, the correspondence between observed and calculated values appears to be sufficiently close to support the general character of the hypothesis as to the relation between the radions of the various species of molecules and the viscosity of the solution. The two sets of viscosities are calculated from *the same formula, with practically the same constants*, the only difference in the constants employed being that the factor γ is taken as 0·032 for KCl and 0·030 for NaCl.

It must be borne in mind that the purpose was not to construct an accurate empirical formula, which is fairly easy where plenty of constants are available. But in the cases examined the simple formula $\eta = C\Sigma\beta r$ is found to be adequate to express, with a near approach to accuracy, the viscosities of the solutions up to normal strength in the case of KCl and 5 per cent. in the case of NaCl, *showing that, with such aqueous solutions, the viscosity depends mainly upon the average size of all the molecules present.*

The departure of the calculated values from the observed values for the NaCl solutions at about normal strength may be partly due to our approximations breaking down before normal strength is reached. But we are more inclined to attribute this departure to a cause which was considered in Part III. (*c*) of this paper. With an autolytic solute, it is probable that there is some *association of the molecules of the solute in* more concentrated solutions. In the case of KCl, with its comparatively small ions and molecules, this does not appear. But in the case of NaCl, with its larger hydrated molecules, the radion of the solute might be notably increased by the

TABLE XXIII.—Viscosity of KCl Solutions, calculated from the Radions.

P.	m.	r_{K}.	r_{Cl}.	V_{K}.	V_{Cl}.	I_{v}.	α.	R.	η observed.	η calculated.	Difference.
0	0	0·01546	0·01528	—	—	7·261	1·0	0·01537	0·01051	0·01051	±
1	0·1347	0·01463	0·01437	3·128	2·968	6·096	0·798	0·01743	0·01050	0·01048	+2
2	0·2712	0·01417	0·01387	2·843	2·671	5·514	0·745	0·01760	0·01047	0.01046	+1
3	0·4094	0·01380	0·01348	2·627	2·448	5·075	0·7095	0·01761	0·01045	0·01044	+1
4	0·5493	0·01348	0·01314	2·448	2·268	4·716	0·6805	0·01757	0·01042	0·01042	±
6	0·8344	0·01293	0·01256	2·163	1·981	4·144	0·639	0·01759	0·01039	0·01040	−1
Normal	1·000	0·01266	0·01227	2·029	1·852	3·881	0·620	0·01720	0·01037	0·01036	+1

TABLE XXIV.—Viscosity of NaCl Solutions calculated from the Radions.

P.	m.	r_{Na}.	r_{Cl}.	V_{Na}.	V_{Cl}.	I_{v}.	α.	R.	η observed.	η calculated.	Difference.
0	0	0·02296	0·01528	12·107	3·569	15·676	1·0	0·02121	0·01051	0·01051	±
1	0·1720	0·02214	0·01422	10·848	2·876	13·724	0·7805	0·02397	0·01068	0·01068	±
2	0·3463	0·02167	0·01365	10·177	2·545	12·722	0·7245	0·02427	0·01083	0·01085	− 2
3	0·5232	0·02129	0·01321	9·648	2·303	11·941	0·685	$0·02438_{5}$	0·01097	0·01100	− 3
4	0·7024	0·02095	0·01282	9·198	2·137	11·335	$0·656_{5}$	0·02435	0·01112	0·01114	− 2
Normal	1·000	0·02047	0·01229	8·578	1·852	10·430	0·620	0·02424	0·01143	0·01132	+11
6	1·068	0·02041	0·01218	8·506	1·806	10·312	0·619	0·02416	0·01150	0·01135	+15

presence of a small fraction of the solute in the form of associated molecules. This, in our view, probably accounts for the observed viscosity values for NaCl in the neighbourhood of 6 per cent. coming out notably higher than the calculated values.

It would be going too far from the purpose of this paper to follow up the considerations which are suggested by the view of the relation of viscosity to molecular size which is here presented. It must suffice to point out that to all the various speculative questions as to the meaning of "negative friction," as to the effect of dissociation in increasing or decreasing friction, and so on, this theory has but one reply—the change in viscosity in aqueous solutions under varying conditions is mainly dependent upon the change in the average molecular size which takes place, that is, to the change in the radions of the components of the solution.

(*g*) *Comparison with* GRÜNEISEN'S *Results*.—The important paper by GRÜNEISEN, which came to hand during the progress of this paper, to which reference has already been made, tends strongly to confirm the propositions here advanced. GRÜNEISEN gives viscosity measurements for some nineteen solutions of electrolytes, and finds that in all cases, as dilution increases, the equivalent viscosity increment comes to a minimum, and then increases with further dilution. This is in accord with our results, according to which, as dilution takes place, ionisation at first *diminishes* the viscosity by breaking up the molecules and afterwards *increases* it, owing to the increase of the ionic radii with further dilution.

Moreover, GRÜNEISEN has dissected the equivalent viscosity increments due to the separate ions at infinite dilution, and has found values of the equivalent viscosity increments for hypothetical "normal solutions of the separate ions." For monovalent ions he finds that these viscosities may be approximately expressed by the equation

$$\eta - 1 = -0{\cdot}207 + 13{\cdot}3/l,$$

where η is the viscosity of a "normal solution of ions" and l is the mobility of such ions. The viscosity of water is reckoned as unity.

This result is not exactly comparable with the present results, but an approximate comparison may be made. If r be the radion of the uncombined water, r' the radion of a set of ions of mobility l, β the fraction of unit volume of the solution occupied by 1 gram-molecule of the ions, we should have, according to our theory, for the viscosity of the hypothetical "normal solution of ions,"

$$\eta = \mathrm{C}\left\{(1-\beta)\, r + \beta r'\right\}.$$

If r_0 be the radion of pure water, we should have $\eta_0 = \mathrm{C}r_0$, and therefore, for the change in viscosity caused by the introduction of 1 gram-molecule of the ions, we should have (remembering that according to our theory $r' = 1/l$)

$$\Delta\eta/\mathrm{C} = (1-\beta)\, r - r_0 + \beta/l.$$

GRÜNEISEN'S expression, for the purpose of comparison, may be written

$$\Delta\eta = -a + b/l.$$

But according to our view, the value of β differs for each ion, and hence GRÜNEISEN'S expression, in which a and b are given constant values for *all* monovalent ions, could only approximately represent the general result, and in fact it does not profess to do more. But the important point is that GRÜNEISEN'S empirical result, which brings out the equivalent viscosity increment of a "normal solution of ions" as approximately a linear function of the reciprocal of the mobility, is in complete accord with and so far confirms the general theory of ionic sizes herein set forth.*

PART VI.—IONIC SIZE IN RELATION TO FREEZING-POINT DEPRESSION.

(*a*) *General Considerations.*—As is well known, the so-called "molecular" freezing-point depression, which is normally nearly constant for dilute solutions of non-electrolytes, varies with the concentration in the case of dilute solutions of electrolytes, and tends at great dilution to a value which is for binary electrolytes about double the value for a dilute solution of non-electrolytes. This may partly be attributed to the ionisation of the electrolyte, upon the theory that the ionisation of a molecule of a binary electrolyte breaks up one molecule into two ions, each of which ions produces the effect of a molecule in the depression of the freezing-point.

Hence, if

Δ = observed freezing-point depression,
N = gram-molecules of solute per 1000 grammes of solvent,
α = ionisation coefficient,

the *effective* number of gram-molecules per 1000 grammes of solvent is $N(1-\alpha)+2N\alpha$, that is to say, $N(1+\alpha)$.

Hence, upon this theory, the true molecular freezing-point depression is $\Delta/N(1+\alpha)$, instead of Δ/N, the ordinary so-called molecular depression. In order to distinguish the fraction $\Delta/N(1+\alpha)$ it will be convenient to refer to it as the "effective molecular freezing-point depression," or more shortly by the initials E.M.D., since upon the ionisation theory $N(1+\alpha)$ is proportional to the actual or *effective* number of molecules present.

When we have evaluated the E.M.D. for any electrolyte, we still find it not constant but variable with the concentration, and it is probable that this variation is intimately connected with the varying ionic volume of the solute, which represents, upon our hypothesis, the varying amount of water in combination with the ions.

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* GRÜNEISEN'S relation for divalent ions is $\eta - 1 = -0\cdot207 + 24/l$. This appears to indicate that divalent ions have a different coefficient of friction from monovalent ions, possibly because they are not approximately spherical.

Now, in order to make a just comparison, we ought to consider the value for the E.M.D. in relation to the ionic volumes in the neighbourhood of the freezing-point. But the data at or near 0° C. necessary for making the comparison accurately do not exist. We have for KCl and NaCl obtained the ionic volumes and the ionisation coefficients at 18° C., and it is probable that the *ratios* of these values will not be sufficiently different at 0° C. to vitiate our comparison, though the values themselves will be sensibly different. We will therefore make a comparison on this basis.

(*b*) *Freezing-point Depression a Linear Function of Ionic Volume.*—JAHN (' Zeit. Phys. Chem.,' 1904, 50, p. 136) gives a series of values of the molecular freezing-point depression for KCl and NaCl which we will use as the basis of our comparison. All his observations are taken in pairs, on solutions of nearly equal concentration. In most cases we have taken the mean of his duplicate observations, but in a few cases the separate results are taken, in order to indicate the order of his maximum errors of observation.

In the following tables are set out for KCl and NaCl the following data :—

N, the number of gram-molecules of the solute per 100 grammes of water,

h, the hydration, *i.e.*, the number of gram-molecules of water per gram-molecule of solute,

r, the radions, of which the cube is calculated from h, as described in Part III. (f),

I_v, the ionic volume, which in our units is equal to the sum of the cubes of the radions $\times 10^6$,

Δ/N, the molecular depression of the freezing-point as given by JAHN,

α, the true ionisation coefficient at 18° C.,

$D = \Delta/N\,(1+\alpha)$, the effective molecular depression of the freezing-point.

TABLE XXV.—KCl.

N.	$h^{-2/3}$.	$r_K^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v.	Δ/N.	α.	D observed.	D calculated.	Difference.
0·3395 0·3377	0·03345 0·03333	2·736	2·561	5·297	3·337 3·344	0·727	1·93 1·94	1·94	− 1 ±
0·259	0·02790	2·870	2·698	5·568	3·37	0·749	1·93	1·93	±
0·201	0·02357	2·981	2·813	5·794	3·385	0·769	1·91	1·92	− 1
0·151	0·01945	3·092	2·929	6·021	3·41	0·790	1·90	1·91	− 1
0·100	0·01483	3·223	3·066	6·289	3·472 3·457	0·819	1·91 1·90	1·90	+ 1 ±
0·076	0·01231	3·298	3·145	6·443	3·485	0·837	1·90	1·89	+ 1
0·0504	0·00938	3·387	3·239	6·626	3·50	0·863	1·88	1·89	− 1
0·0378	0·00774	3·439	3·294	6·733	3·55	0·878	1·89	1·88	+ 1
0·02552 0·02527	0·00596 0·00592	3·511	3·370	6·881	3·547 3·562	0·896	1·87 1·88	1·875	±
∞	—	—	—	7·261	—	—	—	—	—

TABLE XXVI.—NaCl.

N.	$h^{-2/3}$.	$r_{Na}^3 \times 10^6$.	$r_{Cl}^3 \times 10^6$.	I_v.	Δ/N.	α.	D observed.	D calculated.	Difference.
0·301	0·03087	10·339	2·623	12·96	3·40	0·737	1·96	1·96	±
0·2528	0·02748	10·516	2·709	13·23	3·41	0·751	1·95	1·95	±
0·2011	0·02359	10·723	2·813	13·54	3·43	0·769	1·94	1·94	±
0·1505	0·01945	10·952	2·929	13·88	3·44	0·790	1·92	1·93	− 1
0·1004	0·01485	11·210	3·065	14·28	3·46 3·48	0·819	1·90 1·91	1·91	− 1 ±
0·07581	0·01231	11·358	3·144	14·50	3·49	0·837	1·90	1·90	±
0·05035	0·00937	11·531	3·239	14·77	3·50	0·863	1·88	1·89	− 1
0·03798	0·00765	11·634	3·297	14·93	3·55	0·878	1·89	1·89	±
0·02520	0·00591	11·739	3·356	15·10	3·52 3·57	0·896	1·86 1·88	1·88	− 2 ±
∞	—	—	—	15·68	—	—	—	—	—

In the last columns are given the calculated values of D and the differences from the observed values.

In diagrams VIII. and IX. are set out the values of the effective molecular depression as ordinates, upon the values of $(I_\infty - I_v)$ as abscissæ. I_∞ stands for the value of the ionic volume at infinite dilution (see Tables XIII. and XIV.). The values of I_∞ are

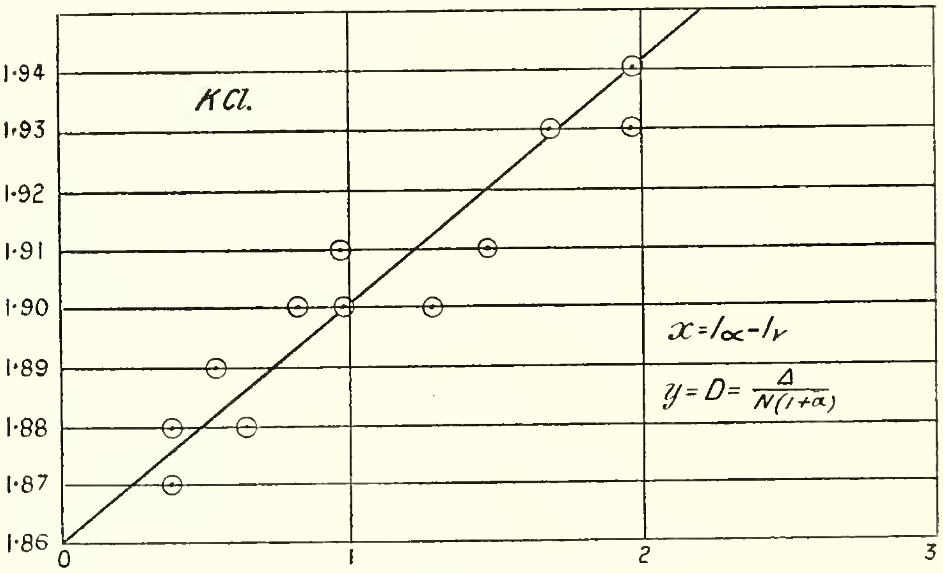

Diagram VIII.

for KCl . . . . $I_\infty = 7·261$,
for NaCl . . . . $I_\infty = 15·68$.

It will be seen at a glance that we have a linear relation between the E.M.D. and the ionic volume, and that *the limiting value of the E.M.D. at infinite dilution is* 1·86, the same value as has been determined for non-electrolytes such as sugar.

The deviations from the straight line are within the limits of experimental error. These limits are indicated by the duplicate values at the dilute ends, which differ by 0·01 in the case of KCl and by 0·02 in the case of NaCl. The expressions which give the values of the E.M.D. are :—

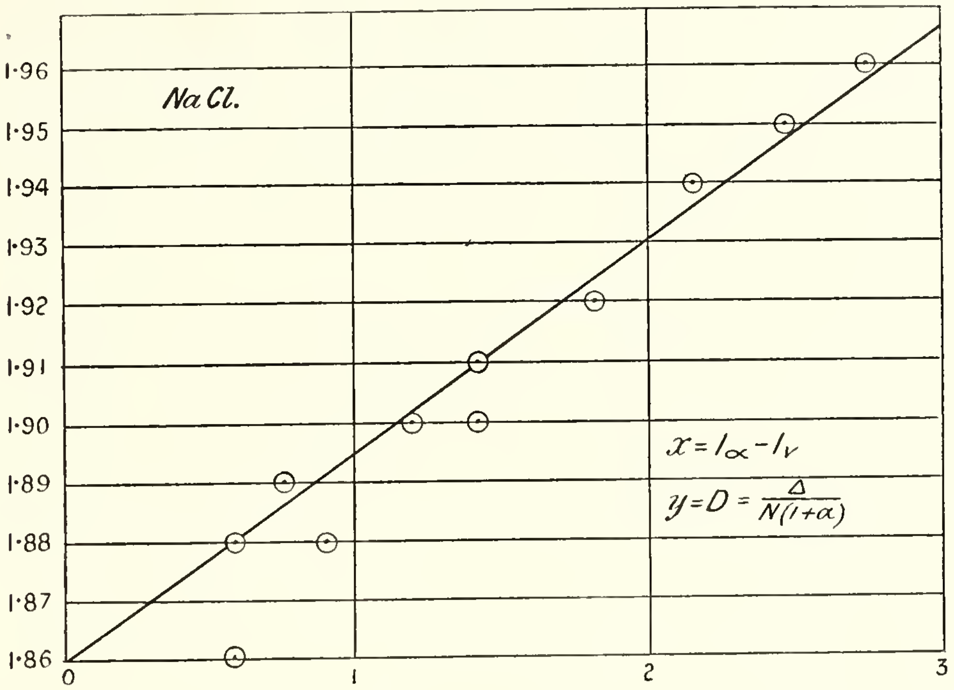

Diagram IX.

For KCl . . . . $D = 1·86 + 0·041\,(I_{\infty} - I_{v})$,

,, NaCl . . . . $D = 1·86 + 0·037\,(I_{\infty} - I_{v})$.

The values of D calculated from these expressions, together with the differences from the observed values, are set out in the last columns of the above tables. The maximum difference in the case of KCl is 0·01, and in the case of NaCl, 0·02, and these are the same as the duplicate experimental differences.

It thus appears that the freezing-point depression, both for electrolytes such as KCl and NaCl, and for non-electrolytes such as sugar in dilute solution, may be expressed by one formula, viz. :—

$$\frac{\Delta}{N(1+\alpha)} = 1·86 + C\,\delta I_{v},$$

since in the case of a non-electrolyte like sugar the ionisation is nil, so that $\alpha = 0$, and the molecular volume is nearly constant in dilute solution,* so that $\delta I_{v} = 0$.

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* We are justified in saying that the molecular volume of sugar is nearly constant in dilute solution owing to the facts :—

(*a*) That the solution volume of sugar in dilute solution is nearly constant.

(*b*) That the viscosity of dilute sugar solutions is almost a linear function of the concentration.

Moreover, the value of C is nearly the same for both KCl and NaCl, though the ionic volumes are very different.

(*c*) *Effective Molecular Freezing-point Depression a Linear Function of Solution Volume.*—In Part IV. (*a*) it was shown that the solution volume was a linear function of the ionic volume, that is the sum of the cubes of the radions, and it has now been shown that the effective molecular freezing-point depression is also a linear function of the ionic volume. If this be so, we can dispense with our hypothesis and obtain the effective molecular freezing-point depression as a linear function of the solution volume.

With the object of testing this relation, the density measurements of KCl and NaCl at 0° C. were made. From these have been already derived formulæ expressing the solution volume in terms of hydration (see Part II. (*c*)). If we denote by δV_s the difference between the solution volume at a given concentration, and the solution volume at infinite dilution, the expressions we obtained in Part II. (*c*) may be written

for KCl . . . . $\delta V_s = 0{\cdot}059\,(1-\gamma)$,
for NaCl . . . . $\delta V_s = 0{\cdot}089\,(1-\gamma)$,

where $\gamma = (1+Bh^{-2/3})^{-3}$, B having the value 6 for KCl and 4 for NaCl. At infinite dilution for KCl, $V_s = 0{\cdot}3068$, and for NaCl, $V_s = 0{\cdot}2125$.

By means of these formulæ we can calculate the solution volumes corresponding to the concentrations at which JAHN's freezing-point observations were made, and we find, as our theory led us to anticipate, that the effective molecular freezing-point depression is in fact a linear function of the solution volume calculated from the densities.

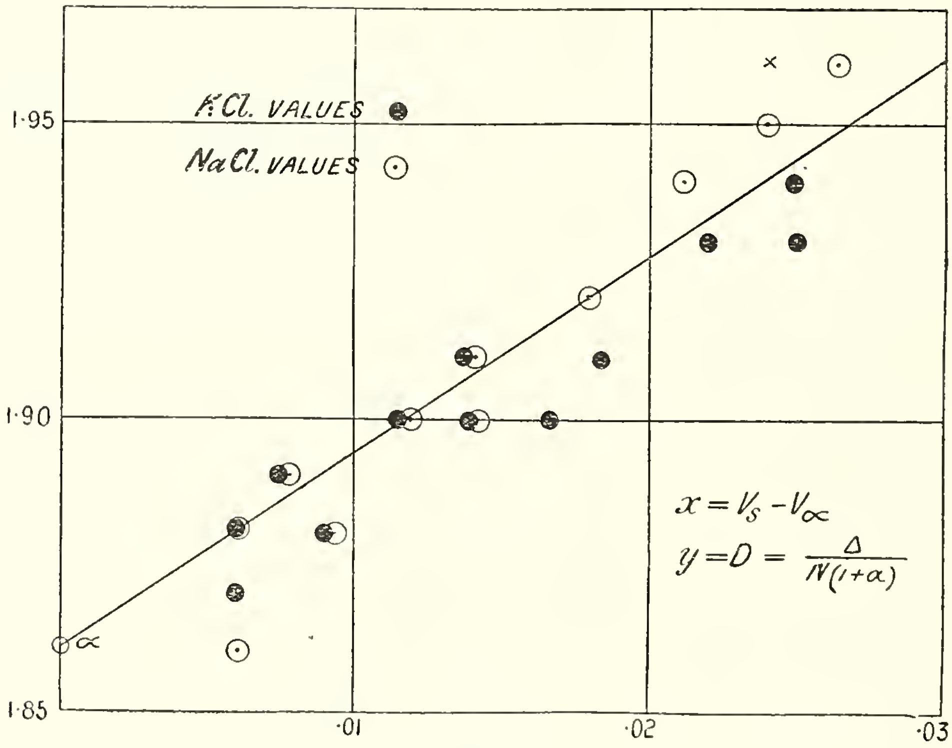

Diagram X.

In the following tables are set out the figures given by JAHN for KCl and NaCl, side by side with the solution volumes calculated from the densities. In Diagram X. are set out the values of the E.M.D., both for KCl and NaCl, as ordinates upon the values of δV_s as abscissæ. The maximum experimental error in the values of the E.M.D. is 0·02, so that within the limits of experimental error we have the E.M.D. a linear function of δV_s. The values of the E.M.D. appear to range a little higher for NaCl than for KCl, as was the case when they were set out upon the ionic volumes. This may represent a real difference, as there is reason to suppose that the density of the water, in combination with the ions and molecules, is slightly different in the two cases. In the comparison with ionic volumes we gave two different expressions, with constants of slightly different value. In the present case we will take one single formula to represent the E.M.D. for both KCl and NaCl, viz., $D = 1{\cdot}86 + 3{\cdot}3\ \delta V_s$.

The calculated values of D are set out in the tables, and the differences from the observed values given in the last columns.

TABLE XXVII.—KCl.

$h^{-2/3}$.	V_s.	δV_s.	D observed.	D calculated.	Difference.
0·03345 0.03333	0·3317	0·0249	1·93 1·94	1·94	−1 ±
0·02790	0·3287	0·0219	1·93	1·93	±
0·02357	0·3251	0·0183	1·91	1·92	−1
0·01945	0·3234	0·0166	1·90	1·91	−1
0·01483	0·3206	0·0138	1·91 1·90	$1{\cdot}90_5$	±
0·01231	0·3182	0·0114	1·90	1·90	±
0·00938	0·3157	0·0089	1·88	1·89	−1
0·00774	0·3142	0·0074	1·89	1·88	+1
0·00596 0·00592	0·3127	0·0059	1·87 1·88	1·88	−1 ±

TABLE XXVIII.—NaCl.

$h^{-2/3}$.	V_s.	δV_s.	D observed.	D calculated.	Difference.
0·03087	0·2388	0·0263	1·96	1·95	+1
0·02748	0·2364	0·0239	1·95	1·94	+1
0·02359	0·2336	0·0211	1·94	1·93	+1
0·01945	0·2304	0·0179	1·92	1·92	±
0·01485	0·2266	0·0141	1·90 1·91	1·91	−1 ±
0·01231	0·2244	0·0119	1·90	1·90	±
0·00937	0·2218	0·0093	1·88	1·89	−1
0·00765	0·2202	0·0077	1·89	1·88	+1
0·00591	0·2185	0·0060	1·86 1·88	1·88	−2 ±

If, as in the comparison with ionic volumes, we take two slightly different constants for KCl and NaCl, we obtain differences between observed and calculated values which are substantially identical with those given in Tables XXV. and XXVI.

Since, in the case of non-electrolytes such as sugar, we have in dilute solutions the solution volume practically constant and the ionisation nil, we arrive again at an expression which is valid both for electrolytes such as KCl and NaCl, and non-electrolytes such as sugar, viz.:

$$\Delta/\mathrm{N}(1+\alpha) = 1{\cdot}86+\mathrm{C}\,\delta\mathrm{V}_s.$$

This result is, of course, quite independent of the hypothesis which it is the purpose of this paper to test, and gives us a ready means of extrapolation for arriving at the true molecular freezing-point depression at infinite dilution based on simultaneous density observations.

Whether expressed in terms of ionic volumes (according to our hypothesis) or in terms of solution volumes, the meaning of the relation seems to be clear. Both $\delta\mathrm{I}_v$ and $\delta\mathrm{V}_s$ are proportional to the decrease in the amount of water in combination with a given weight (say a gramme equivalent) of the solvent as concentration increases. Hence we get the result that in dilute solutions *the increment of the effective molecular depression of the freezing-point above* 1·86 *as concentration increases is proportional to the decrement of the amount of water in combination with a gram-molecule of the solute.* To discuss the physical meaning of this relation would carry us too far from the main lines of the present paper.

(*d*) *Correction of Freezing-point Depression by Reference to Ionic Volumes.*—In Part V. (*f*) our experimental results were shown to lead to the view that the viscosity of an aqueous solution was proportional to the average molecular size of all the molecules. We were able also to calculate approximately from the viscosity data the actual volume occupied by a gramme equivalent of the solute at a given concentration. If I_v be the ionic volume at a given concentration, and the volume in litres of a gramme equivalent of ions be taken as $\gamma\mathrm{I}_v$, it was found in the case of KCl, from the viscosity data, that $\gamma = 0{\cdot}032$. Hence the volume of a gramme equivalent of KCl in solution is $32\mathrm{I}_v$, reckoned in cubic centimetres.

To find the volume of the KCl itself, we have the density of solid fused KCl which is given by QUINCKE as 1·87, which gives for the volume of 1 gramme of liquid KCl 0·551 cub. centims., allowing 3 per cent. for expansion from the solid to the liquid state. This gives the volume of a gramme equivalent of liquid KCl as 41·1 cub. centims., and therefore the volume of water combined with 1 gramme equivalent of KCl is

$$32\mathrm{I}_v-41{\cdot}1 \text{ cub. centims.}$$

Hence, if we have a solution of KCl containing N gram-molecules dissolved in 1000 grammes water, we have approximately for the amount of free water

$$w = 1000-\mathrm{N}(32\mathrm{I}_v-41{\cdot}1).$$

Let us now calculate the effective molecular freezing-point depression, not upon the *total* amount of water present but upon the amount of *free* water obtained from the above expression. The expression for the E.M.D. calculated in this way is

$$D' = \frac{\Delta}{N'(1+\alpha)},$$

where N′ is the number of gram-molecules of the solute in 1000 grammes of *free* water. We have then

$$N' = \frac{1000N}{w} \quad \text{and} \quad D' = D \cdot \frac{w}{1000}.$$

In the following table are set out the values of D resulting from Jahn's data (taken from the column "D calculated" in Table XXV.), together with the other data necessary for the calculation of D′, the effective molecular depression of the freezing-point calculated on the amount of free water. It will be seen that we obtain *a constant value* for D′, up to about twice decinormal solutions, the mean value of the constant being 1·867.

Table XXVIIIa.

N.	I_v.	w.	D.	D′.	Difference from mean.
		grammes.			
0·201	5·794	971	1·92.	1·864	− 3
0·151	6·021	977	1·91	1·866	− 1
0·100	6·289	984	1·90	1·869	+ 2
0·076	6·443	987·5	1·89	1·866	− 1
0·0504	6·626	991	1·89	1·873	+ 6
0·0378	6·733	993	1·88	1·867	±
0·0254	6·881	995	1·875	1·866	1

We may recapitulate the method by which the above figures are obtained. The ionic volumes measured in arbitrary units having only relative values were deduced from the corrected conductivity data. The factor γ which was required to give us the absolute volume for a gramme equivalent of KCl in solution, with its combined water, was deduced from the viscosity data. The volume of free water so deduced, when applied to calculate the effective molecular freezing-point depression, gives us for this *a constant value*, which is in correspondence with the value obtained for non-electrolytes. We thus obtain a striking confirmation of the validity of the hypothesis and of the method pursued, and at the same time illustrate the dependence of the various physical properties considered upon the varying size of the hydrated ions caused by the varying amount of water with which they combine.*

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* The corresponding values for NaCl solutions give the constant as 1·860 for high dilutions, but for lower dilutions the value is too low, indicating over-correction. This may indicate that either the ionic volumes deduced for NaCl, or the value 0·030 for γ, may be slightly too high. The larger ionic volume for the Na ion renders any error much more effective in disturbing the constant.

PART VII.—IONIC SIZE IN RELATION TO REFRACTIVE POWER.

The refractive power of a medium is known to be closely related to the state of aggregation of its components. According to the hypothesis which we are discussing, the combination of water with the ions and molecules of a solute changes the state of aggregation of the fraction of the water which is so combined, and also, to some extent, of the uncombined water. Hence we should expect to find a close relation between ionic volume and refractive power.

If n = refractive index of a solution at 18° C.,
n_0 = refractive index of water at same temperature,
m = concentration (gramme equivalents per litre of solution),

the simplest measure of the refractive power is $(n-n_0)/m$, say $\Delta n/m$, which we may refer to shortly as the equivalent refractive power of the solute.

A recent paper by DINKHAUSER ('Sitz.-Ber., Wien. Akad. Wiss.,' July, 1905, p. 1001) gives the values of this equivalent refractive power for solutions of KCl and NaCl. The values for KCl appear to be a little rough, but the values for NaCl seem to be particularly accurate.*

In the following tables are given the concentrations, the values of log h and of the radions and ionic volumes calculated therefrom, together with the values of the equivalent refractive power given by DINKHAUSER. In Diagrams XI. and XII. are set out the values of the equivalent refractive power as ordinates upon the values of the ionic volumes as abscissæ. It will be seen that a linear relation appears, which may be expressed by the equations

for KCl . . . . $\Delta n/m = 0{\cdot}009145 + 0{\cdot}0001845\ I_v$,
for NaCl . . . . $\Delta n/m = 0{\cdot}00855\ + 0{\cdot}0001271\ I_v$.

The values calculated from these expressions and the differences from observed values are also given in the tables. If I_∞ be the value of I_v at infinite dilution (see Tables XIII. and XIV.), and we put $\Delta I_v = I_\infty - I_v$, the expressions may be written

for KCl . . . . $\Delta n/m = 0{\cdot}01048 - 0{\cdot}0001845\ \Delta I_v$,
for NaCl . . . . $\Delta n/m = 0{\cdot}01054 - 0{\cdot}0001271\ \Delta I_v$.

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* For KCl, DINKHAUSER gives the value 9·80 for m = 1·234 (p. 1020) and the same value for m = 1 (p. 1025). The whole series shows that the latter value must be inaccurate. For m = 0·812 he gives the value 10·06 (p. 1020) and for m = 0·5 the value 10·05. The former of these values is rejected. The values for concentrations less than one-fiftieth normal are also rejected, since the large factor by which the observed value of n must be multiplied to get the equivalent refractive power greatly magnifies any error. These discrepancies are partly due to the fact that DINKHAUSER has combined his own results with those of other observers.

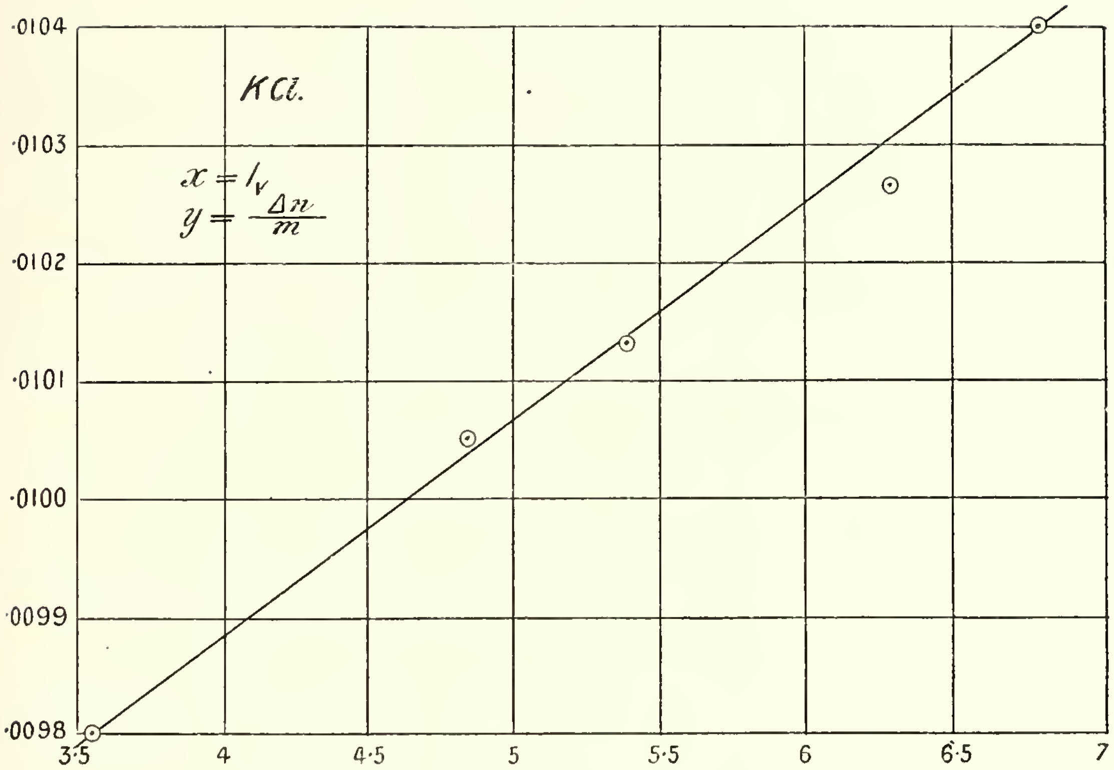

Diagram XI.

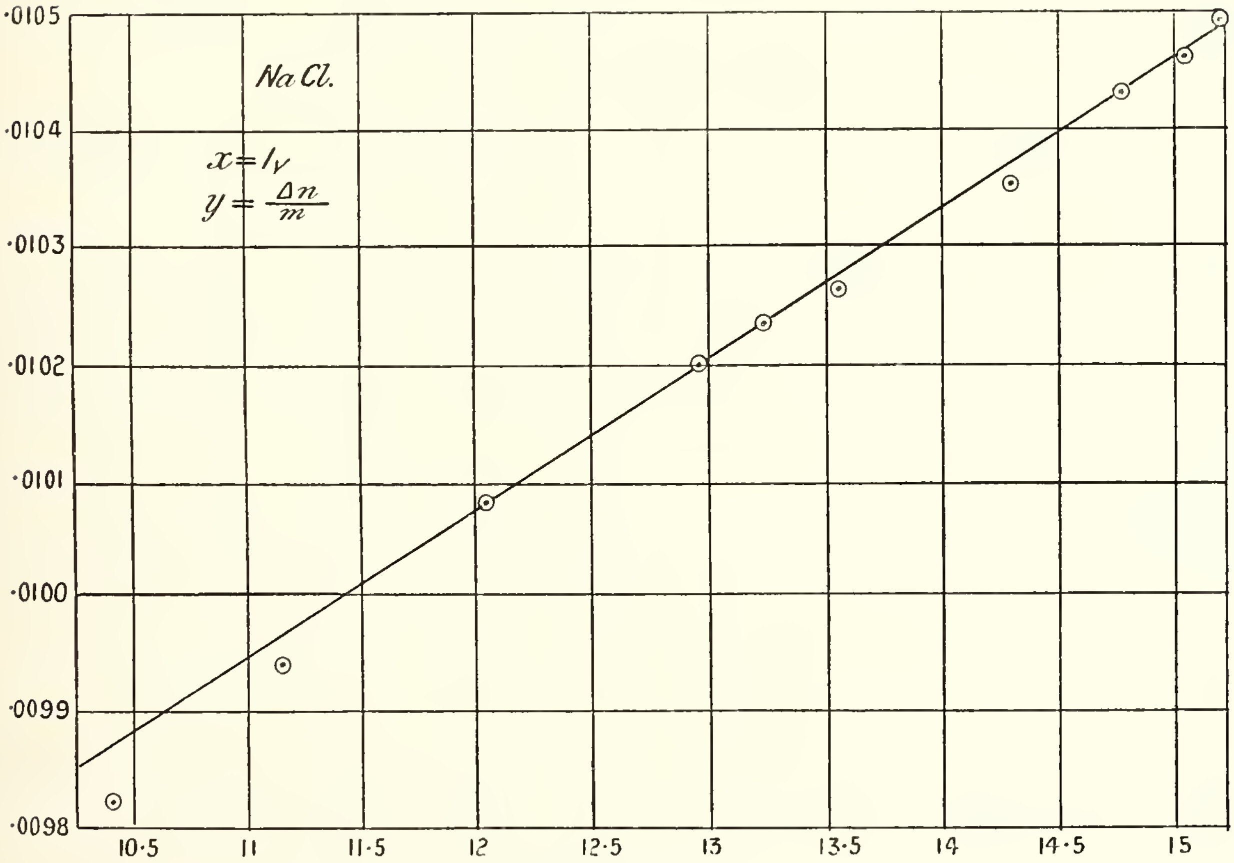

Diagram XII.

Table XXIX.—KCl.

m.	log h.	r_K^3.	r_{Cl}^3.	I_v.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·03	3·26629	3·474	3·331	6·805	0·0104	0·0104	±
0·1	2·74257	3·222	3·065	6·287	0·01026	0·01030	− 4
0·311	2·24734	2·775	2·601	5·376	0·01013	0·01014	− 1
0·5	2·03874	2·508	2·328	4·836	0·01005	0·01004	+ 1
1·234	1·63710	1·866	1·687	3·553	0·00980	0·00980	±

Table XXX.—NaCl.

m.	log h.	r_{Na}^3.	r_{Cl}^3.	I_v.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·02	3·44259	11·798	3·385	15·18	0·01049	0·01048	+ 1
0·03	3·26646	11·694	3·331	15·03	0·01046	0·01046	±
0·05	3·04444	11·532	3·240	14·77	0·01043	0·01043	±
0·1	2·74304	11·211	3·066	14·28	0·01035	0·01036	− 1
0·2	2·44131	10·725	2·813	13·54	0·01026	0·01027	− 1
0·25	2·34404	10·521	2·712	13·23	0·01023	0·01023	±
0·3	2·26451	10·336	2·622	12·96	0·01020	0·01020	±
0·5	2·04105	9·711	2·331	12·04	0·01008	0·01008	±
0·75	1·86290	9·089	2·062	11·15	0·00994	0·00997	− 3
1·0	1·73590	8·578	1·852	10·43	0·00982	0·00988	− 6

Table XXX. shows that the relation in the case of NaCl down to half normal solutions is particularly accurate.

In Part IV. (*b*) it was shown that the ionic volume might be calculated from the radions of the separate ions with fair accuracy down to nearly normal solutions. It is obvious, however, that, as the proportion of un-ionised solute becomes greater, it becomes more and more inaccurate to take the ionic volume of a molecule as the sum of the volumes of a pair of ions. It is probable that the divergence of the calculated values in Table XXX. for the last two observations tabulated is due to this error in the calculation of the ionic volumes. Now, as in the case of freezing-point depression, so here, having shown previously that solution volume is a linear function of ionic volume, we deduce that the equivalent refractive power, which is shown above to be a linear function of ionic volume, must therefore also be a linear function of solution volume. The series of values given by Dinkhauser for KCl is not sufficiently good to make this comparison useful. But the series for NaCl shows clearly the remarkable fact that the equivalent refractive power is *accurately a linear function of the solution volume right through the range of dilute and concentrated solutions.*

In Table XXXI. are set out the solution volumes, calculated from the density data given by DINKHAUSER,* the values of the equivalent refractive power as given by him, together with the values calculated from the linear relation

$$\Delta n/m = 0{\cdot}01643 - 0{\cdot}0215\,V_s.$$

It will be seen that the difference between observed and calculated values nowhere exceeds more than a unit in the last place of decimals, from a concentration of one-tenth normal to five times normal.

It may be noted that we have here a clue which may enable us to obtain the ionic volume in concentrated solutions.† In dilute solutions we have shown that the ionic volume, as derived from the radions, is a linear function of the solution volume. It seems probable that this linear relation persists through concentrated solutions, and that the solution volume may therefore enable us to calculate accurately the ionic volume in concentrated solutions. But we cannot follow up this clue in the present paper.

TABLE XXXI.—NaCl.

m.	V_s.	$\Delta n/m$ observed.	$\Delta n/m$ calculated.	Difference.
0·1	0·2831	0·01035	0·01034	+1
0·25	0·2888	0·01023	0·01022	+1
0·5	0·2960	0·01008	0·01007	+1
0·75	0·3016	0·00994	0·00995	−1
1·0	0·3071	0·00982	0·00983	−1
2	0·3235	0·00946	0·00947	−1
3	0·3350	0·00922	0·00923	−1
4	0·3461	0·00898	0·00899	−1
5	0·3567	0·00876	0·00876	±

PART VIII.—CONCLUDING OBSERVATIONS.

Let us now briefly review the main course of the argument, as developed in this and the former paper, in relation to our fundamental hypothesis.

As our starting point we took the Van 't Hoff dilution law, which we may express by saying that if D represents the concentration of the dissociated portion of a solute and U the concentration of the undissociated portion, reckoned by means of the

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* DINKHAUSER gives the values of $\Delta\rho/m$, where $\Delta\rho$ is the difference of the density ρ of the solution from the density ρ_0 of water at the same temperature, and m is the concentration. The solution volumes can be calculated from the expression

$$V_s = \frac{1}{\rho_0}\left(1 - \frac{\Delta\rho}{m} \cdot \frac{10^3}{E}\right),$$

where E is the weight of a gram-molecule of the solute.

† It would be more accurate in concentrated solutions to use the term molecular volume instead of ionic volume, but unfortunately the term molecular volume has been already misapplied to indicate the product of the solution volume by the weight of a gram-molecule—a use which has led to much confusion of ideas.

ordinary value of α, there exists a linear relation between log D and log U, leading to a relation of the form $K = D/U^n$, where n is for various electrolytes nearly but not quite two thirds. (See Appendix.)

This suggested that if we could find a suitable correction for α, which is usually taken as λ/Λ, the Van 't Hoff dilution law would turn out to be an *exact* relation for dilute solutions of binary electrolytes such as KCl.

The materials for such a correction were sought in the known fact that the viscosity of the solution produced aberrations in the mobilities of the ions, but viscosity differences alone were inadequate to give an account of such aberrations.

KOHLRAUSCH'S observations on the temperature coefficients of the ions had already led him to the general view that the ions must be considered to be water-coated. This water combination necessarily altered the sizes of the ions, and it was considered that the joint effect of changes of viscosity and changes of size might adequately account for changes in the mobility.

To reckon these effects quantitatively, STOKES' theorem as to the motion of a small sphere in a viscous medium was available, and though the actual motion of the ions through an electrolyte under the influence of a potential gradient is probably extremely erratic, it was thought that, nevertheless, the effect of size and viscosity upon the average rectilinear drift under the influence of the electro-motive force might be amenable to exact treatment, just as the average rectilinear drift itself can be accurately calculated.

Assuming, then, that the aberrations of the mobilities which made the Van 't Hoff law inexact were due to such causes and could be dealt with in this way, corrections were applied to the mobilities, and corrections for α were calculated, the nature of which was determined by the Stokes theorem, and the amount of which was determined by the Van 't Hoff law (expressed in terms of the hydration h instead of the volume V of the solution).

The result of this process was to give us the expression

$$r = r_{\infty}(1 + Bh^{-2/3})^{-1}$$

for the relation betwen the radius of an ion and the dilution of the solution.

Up to this point, if one may compare small things with great, the process followed is similar to that of the astronomer who sought to locate the position of a new planet by considering the irregularities produced in the movements of the old ones. In that case the result could be tested by turning a telescope to the spot indicated by the calculations.

In the present case the result could only be tested by considering how far the hypothesis as to the changing sizes of the ions owing to the changes in the amount of water combination could be rationally related to the various physical phenomena of solutions, and how the quantitative results were functionally related to existing data. In the case of each set of phenomena it was necessary to consider *à priori* how the changing size of the ions would be likely to affect it. *À priori* it seemed probable that the Hittorf transference numbers, and the viscosities of the solutions themselves, would depend merely upon the linear dimensions of the ions, whilst the densities of the solutions and the variations of effective molecular freezing-point depression and refractive power would depend upon the amounts of combined water, and therefore upon the cubes of the ionic dimensions.

These *à priori* considerations have, in fact, turned out to be justified, not merely qualitatively, but with considerable numerical accuracy, having regard to the difficulty of some of the approximations involved. We are able to express the Hittorf numbers, the densities, the effective molecular freezing-point depressions and the equivalent refractive power within the limits of experimental error, as simple functions of the radions, and to express the viscosities, with a fair approach to accuracy, not merely as a function of the radions of the solute, but also upon the extended conception of the radion as being simply proportional to the radion, or average molecular radius, of the whole solution. Our hypothesis has also enabled us to discover new relations which are independent of the hypothesis, viz., the fact that the Hittorf migration numbers are a linear function of $(B+h^{2/3})^{-1}$, and the fact that the effective molecular freezing-point depression and the equivalent refractive power are linear functions of the solution volume.

It is submitted that the above considerations justify the working hypothesis, that the function which we have named the radion, derived as above described, may in fact be taken to be a measure of the actual sizes of the ions. In any case, the radion turns out to be of fundamental importance in correlating the various phenomena of solution.

APPENDIX.

Note on the Van 't Hoff Law.

Reasons for Supposing that the Van 't Hoff Law with Index exactly $\frac{2}{3}$ is an Accurate Law for certain Binary Electrolytes with Monovalent Ions.

1. A large number of such electrolytes follow the Van 't Hoff law with close approximation over a considerable range of dilution. (See Bancroft, 'Zeit. Phys. Chem.,' 31, 191, 1899, and for KCl see Bousfield, 'Zeit. Phys. Chem.,' 53, p. 268, 1905, where diagram for KCl is given.)

For KCl the value of the index is $\frac{2\cdot 2}{3\cdot 2}$ for uncorrected α.

2. In order to test the law with great accuracy, we ought to examine it over a range of dilutions so high that the viscosity is practically constant and the increase of ionic size (if any) is practically complete. In such a case we might expect to find the value of n practically constant and equal to $\frac{2}{3}$, if the Van 't Hoff law holds accurately. It is impossible to make such a test, owing to the fact that the error introduced by the uncertainty as to the correction for the conductivity of the solvent, multiplied by the

large factor necessary to obtain the equivalent conductivity, entirely swamps the small difference (if any) from the exact value of the index which we desire to detect.

Hence the only available means of investigation is to get the true value of n at high dilutions, by extrapolation from lesser dilutions where the errors to which reference is made above become almost inappreciable. For this purpose a range of dilutions is chosen between $\frac{1}{10}$ normal and $\frac{1}{1000}$ normal. As we descend through this range of dilutions (from higher to lower dilution) we necessarily get an increasing divergence from the true value of n, owing to changes of viscosity and changes of ionic size, but we can extrapolate into the desired region where viscosity and ionic size are nearly constant.

According to the Van 't Hoft law, in the modified form adopted in this paper, if $x = \log \frac{h}{1-\alpha}$, $y = \log \frac{h}{\alpha}$, we ought to have $dy/dx = \frac{2}{3}$.

In the following tables are set out the values of α (uncorrected, that is to say

TABLE XXXII.—KCl.

m.	$\alpha = \frac{\lambda}{\Lambda}$.	$\log h$.	$y = \log \frac{h}{\alpha}$.	$x = \log \frac{h}{1-\alpha}$.	$\frac{\Delta y}{\Delta x}$.	$\frac{\Delta y}{\Delta x} - \frac{2}{3}$.
0·0005	0·9847	5·04477	5·0515	6·8601		
					0·674	0·007
0·001	0·9788	4·74374	4·7531	6·4174		
					0·678	0·011
0·002	0·9709	4·44270	4·4555	5·9788		
					0·681	0·014
0·005	0·9563	4·04474	4·0642	5·4043		
					0·683	0·016
0·01	0·9411	3·74367	3·7700	4·9736		
					0·691	0·024
0·02	0·9221	3·44248	3·4777	4·5509		
					0·697	0·030
0·05	0·8897	3·04419	3·0950	4·0016		

TABLE XXXIII.—NaCl.

m.	$\alpha = \frac{\lambda}{\Lambda}$.	$\log h$.	$y = \log \frac{h}{\alpha}$.	$x = \log \frac{h}{1-\alpha}$.	$\frac{\Delta y}{\Delta x}$.	$\frac{\Delta y}{\Delta x} - \frac{2}{3}$.
0·001	0·9771	4·74375	4·7538	6·3839		
					0·674	0·007
0·002	0·9684	4·44271	4·4566	5·9430		
					0·676	0·009
0·005	0·9522	4·04475	4·0660	5·3653		
					0·679	0·012
0·01	0·9354	3·74368	3·7727	4·9335		
					0·684	0·017
0·02	0·9140	3·44259	3·4816	4·5081		
					0·693	0·026
0·05	0·8782	3·04444	3·1009	3·9588		

$\alpha = \lambda/\Lambda$), the values of x and y calculated therefrom and the values of $\Delta y/\Delta x$. In diagram XIII. are set out the values of $\Delta y/\Delta x - \frac{2}{3}$ as ordinates, upon the values of α as abscissæ. Each value of $\Delta y/\Delta x$ belongs to a value of α intermediate between the two values of α from which it is reckoned. As this intermediate value is uncertain, each value of $\Delta y/\Delta x - \frac{2}{3}$ is set out *twice*, *i.e.*, to say upon the two values of α which lie one on each side of it. It will be seen from the diagrams that when $\alpha = 1$, *i.e.*, at infinite dilution, the extrapolated value of $\Delta y/\Delta x - \frac{2}{3}$ is in each case zero, *i.e.*, $dy/dx = \frac{2}{3}$ accurately.

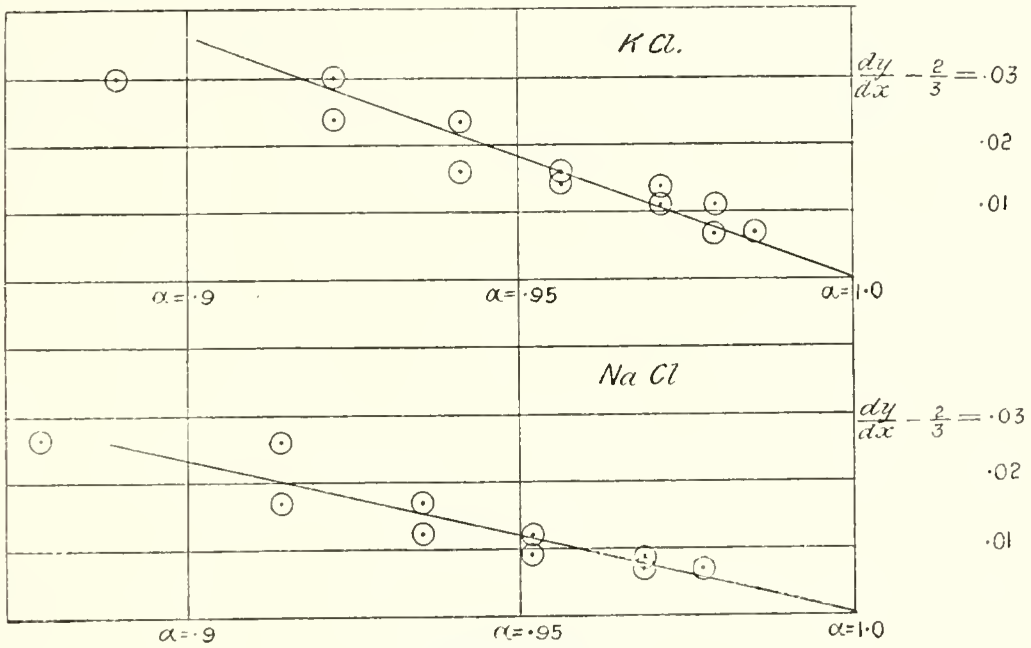

Diagram XIII.

This enables us to say that in the region of dilution where change of viscosity and ionic size become negligible the Van 't Hoff law holds accurately for KCl and NaCl.

If we were to follow out the same process for (say) acetic acid, we should find that the limiting value of dy/dx was accurately $\frac{1}{2}$, *i.e.*, we should get OSTWALD's law.

3. OSTWALD's law, with its accurate index, can be easily derived from the law of mass action. There is, therefore, reason to suppose that the Van 't Hoff law should also be capable of being based upon the law of mass action, which would necessarily give us, for high dilution, some definite and exact value for the index, since the index is the ratio of certain small numbers of molecules, which are necessarily whole numbers. In the former paper (see 'Zeit. Phys. Chem.,' 53, p. 266, 1905) this matter was discussed, and a hypothesis was set out upon which the law of mass action gives the Van 't Hoff law with exact index. This hypothesis may be unsound, but it shows the possibility of basing the Van 't Hoff law upon the law of mass action when the nature of the equilibrium between the molecules of solvent and solute is better understood.

MORGAN and KANOLT ('Journ. Amer. Chem. Soc.,' 26, p. 635, 1904) have arrived at a similar result, based upon the law of mass action, with a wholly different hypothesis as to combination of ions and water molecules.

Again, this hypothesis may not be accurate, but it strengthens the view that the Van 't Hoff law can, in some way, be based on the law of mass action, which would give an exact instead of an approximate index.

The above sets of considerations point to the view, that if α, the coefficient of ionisation, be corrected for viscosity and ionic size, the Van 't Hoff law would hold accurately in the lower range of dilution. It is found that such a correction can be made by the aid of STOKES' theorem, according to which the velocity of transportation is inversely proportional to the linear dimensions of the ionic complex, which gives the ionic size as a simple function of dilution.

The relation above indicated should be expressible by the equation

$$\frac{dy}{dx} - \tfrac{2}{3} = k(1-\alpha),$$

when $1-\alpha$ is small. This equation can be compared with the relation

$$h(1-\alpha)^2/\alpha^{3(1+n)} = \mathrm{C} \quad \ldots \ldots \ldots \ldots \quad (1).$$

Since for considerable dilution h is proportional to $1/m$, the relation may be written as

$$(1-\alpha)/\alpha^p = \mathrm{B}m^{1/2} \quad \ldots \ldots \ldots \ldots \quad (2).$$

This is the relation given by KOHLRAUSCH as an empirical result ('Sitz. Akad. Wiss. Berlin,' 1900, p. 1006). It is shown by him to hold with great accuracy from decinormal to infinite dilution for a series of nine binary electrolytes with monovalent ions, and is used by him to deduce the values of Λ_∞.

As equation (1) is thus established as an adequate empirical relation, we may use it by a reverse process to examine the more exact relation which the diagram indicates when the curve is prolonged.

Equation (1) may be written

$$3\log\frac{h}{\alpha} - 2\log\frac{h}{1-\alpha} = \log \mathrm{C} + 3n\log\alpha.$$

Using Napierian logarithms and writing μ for the modulus of common logarithms,

$$\frac{x}{\mu} = \log\frac{h}{1-\alpha}, \quad \frac{y}{\mu} = \log\frac{h}{\alpha} \quad \ldots \ldots \ldots \ldots \quad (3),$$

and we may write the relation as

$$3y - 2x = \log \mathrm{C} + 3\mu n \log\alpha.$$

By differentiation we get

$$\frac{dy}{dx} - \tfrac{2}{3} = n \cdot \frac{\mu}{\alpha} \cdot \frac{d\alpha}{dx} \quad \ldots \ldots \ldots \ldots \quad (4).$$

Also from (3) we get by eliminating the variable h and differentiating

$$\frac{\mu}{\alpha} \cdot \frac{d\alpha}{dx} = \left(1 - \frac{dy}{dx}\right)(1-\alpha),$$

whence by substituting in (4) and writing

$$\frac{dy}{dx} - \tfrac{2}{3} = z, \quad 1-\alpha = \beta,$$

we obtain the equation

$$z = n\beta\left(\tfrac{1}{3} - z\right) \quad \ldots \ldots \ldots \ldots \quad (5).$$

This, then, is the more exact equation of the curve which has been indicated as a straight line in the diagram on p. 157. The curve starts from the origin, and has a horizontal asymptote.

To compare the constants with KOHLRAUSCH'S figures, we note that

$$p = \tfrac{3}{2}(1+n), \quad \text{or} \quad n = \tfrac{2}{3}p - 1.$$

For p KOHLRAUSCH gives the values

$$\text{KCl}, \; p = 3 \cdot 280, \quad \text{NaCl}, \; p = 2 \cdot 649,$$

which gives for n the values

$$\text{KCl}, \; n = 1 \cdot 187, \quad \text{NaCl}, \; n = 0 \cdot 766.$$

For the tangent of the inclination of the curve at and near the origin we have for KCl the value 0·39, and for NaCl the value 0·25.

These agree well with the diagram.

The accurate empirical law deduced by KOHLRAUSCH is, in fact, not sensibly different in the part near the origin $\alpha = 1$ from the Van 't Hoff law for which $p = \frac{3}{2}$. That is, in the region where, from the present point of view, ionic size and viscosity may be regarded as constant, VAN 'T HOFF'S law, there equivalent practically to $1 - \alpha = \text{const} \times m^{1/2}$, is to be taken as the starting point for substances of the class here considered.

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ON THE FIGURE AND STABILITY OF A LIQUID SATELLITE

BY

SIR G. H. DARWIN, K.C.B., F.R.S.,
PLUMIAN PROFESSOR AND FELLOW OF TRINITY COLLEGE, CAMBRIDGE.

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By Sir G. H. Darwin, *K.C.B., F.R.S., Plumian Professor and Fellow of Trinity College, Cambridge.*

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PREFACE.

MORE than half a century ago ÉDOUARD ROCHE wrote his celebrated paper on the form assumed by a liquid satellite when revolving, without relative motion, about a solid planet.* In consequence of the singular modesty of ROCHE'S style, and also because the publication was made at Montpellier, this paper seems to have remained almost unnoticed for many years, but it has ultimately attained its due position as a classical memoir.

The laborious computations necessary for obtaining numerical results were carried out, partly at least, by graphical methods. Verification of the calculations, which as far as I know have never been repeated, forms part of the work of the present paper. The distance from a spherical planet which has been called "Roche's limit" is expressed by the number of planetary radii in the radius vector of the nearest possible infinitesimal liquid satellite, of the same density as the planet, revolving so as always to present the same aspect to the planet. Our moon, if it were homogeneous, would have the form of one of ROCHE'S ellipsoids; but its present radius vector is of course far greater than the limit. ROCHE assigned to the limit in question the numerical value 2·44; in the present paper I show that the true value is 2·455, and the closeness of the agreement with the previously accepted value affords a remarkable testimony to the accuracy with which he must have drawn his figures.

He made no attempt to obtain numerical solutions except in the case of the infinitely small satellite. In this case the figure is rigorously ellipsoidal, but for a finite satellite this is no longer the case; nor do his equations afford the means of determining exactly the ellipsoid which most nearly represents the truth. These deficiencies are made good below, and we find that even in the extreme case of two equal masses in limiting stability the ellipsoid is a much closer approximation to accuracy than might have been expected.

It is natural that ROCHE, writing as he did half a century ago, should not have been in a position to discuss the stability of his solutions with completeness, and although he did much in that direction he necessarily left a good deal unsettled.

In 1887 I attempted the discussion of some of the problems to which this paper is devoted, by means of spherical harmonic analysis.† POINCARÉ'S celebrated memoir on figures of equilibrium‡ was published just when my work was finished, and I kept my paper back for a year in order to apply to my solutions the principles of stability enounced by him. The attempt is given in an appendix to my paper, but unfortunately I failed to understand his work completely, and my investigation, as it stands, is erroneous from the fact that one term in the energy is omitted.* I think, however, that the defect may easily be made good.

---

* "La figure d'une masse fluide soumise à l'attraction d'un point éloigné," 'Acad. des Sci. de Montpellier,' vol. 1, 1847–50, p. 243.

† "Figures of Equilibrium of Rotating Masses of Fluid," 'Phil. Trans. Roy. Soc.,' vol. 178 (1887) A, pp. 379–428.

‡ "Sur l'équilibre d'une masse fluide animée d'un mouvement de rotation," 'Acta. Math.' 7 : 3, 4 (1885), pp. 259–380.

The analysis of the present paper is carried out by means of ellipsoidal harmonic analysis. In the course of the work it becomes necessary to refer to previous papers by myself, all published in the 'Philosophical Transactions'; they are: "Ellipsoidal Harmonic Analysis," vol. 197 (1901) A, pp. 461–557; "The Pear-Shaped Figure of Equilibrium of a Rotating Mass of Liquid," vol. 198 (1902) A, pp. 301–331; "The Stability of the Pear-Shaped Figure of Equilibrium, &c.," vol. 200 (1903) A, pp. 251–314; "The Integrals of the Squares of Ellipsoidal Surface Harmonic Functions," vol. 203 (1904) A, pp. 111–137. These papers are hereafter referred to by the abridged titles "Harmonics," "The Pear-Shaped Figure," "Stability," and "Integrals."

The analysis involved in the investigation is unfortunately long and complicated, but the subject itself is not an easy one, and the complication was perhaps unavoidable.

The principal inducement to attack this problem was the hope that it might throw further light on the form of the pear-shaped figure in an advanced stage of development when it might be supposed to consist of two bulbs of liquid joined by a very thin neck. The arguments adduced below seem to show that such a figure must be unstable.

M. LIAPOUNOFF has recently published a paper in which he states that he is able to prove the instability of the pear-shaped figure even when only infinitesimally furrowed.† In view of my previous work on the stability of this figure, and from other considerations it seems very difficult to accept the correctness of this result.

At the end a summary is given of the conclusions arrived at, and this last subject is discussed amongst others.

PART I.—ANALYSIS.

§ 1. *The Stability of Liquid Satellites.*

This paper deals with two problems concerning liquid satellites which possess so much resemblance that I did not for some time perceive that there is an essential difference between them. One of these is the determination of the figures and of the secular stability of two masses of liquid revolving about one another in a circular orbit without relative motion of their parts. We may refer to this as the problem of

---

[*] This is the term denoted $\frac{1}{2}\omega^2(\delta I)^2/I$ below.

[†] "Sur un problème de Tchebychef," 'Acad. Imp. des Sci. de St. Pétersbourg,' vol. 17, No. 3 (1905).

"the figures of equilibrium"; the other may be called "ROCHE's problem," and it differs only from the former in that one of the two masses of liquid is replaced by a particle or by a rigid sphere. However, in the numerical solutions found hereafter, ROCHE's problem is slightly modified, for the rigid sphere is replaced by a rigid ellipsoid of exactly the same form as that assumed by the other mass of liquid in the problem of the figures of equilibrium. Thus, with this modification, the two problems become identical as regards the shape of the figures; but, as we shall see, they differ widely as to the conditions of secular stability. This difference arises from the fact that in the one case there are two bodies which may be subject to tidal friction, and in the other there is only one.

If in either problem there is no solution when the angular momentum has less than a certain critical value, if for that value there is one solution and for greater values there are two, then the principle of POINCARÉ shows that the single solution is the starting point of a pair of which one has one fewer degrees of instability than the other. If, then, one of the two solutions is continuous with a solution which is clearly stable, it follows that the determination of minimum angular momentum will give us the limiting stability of that solution; and this is the point of greatest interest in all such problems.

Our two problems differ in the value of the angular momentum of which the minimum has to be found. For, if in ROCHE's problem the second body is a particle, it has only orbital momentum; if the second body is a sphere, it must be deemed to have no rotation; and, finally, in the modified form of the problem, the rotational momentum of the rigid body must be omitted from the angular momentum, which has to be a minimum for limiting stability.

It will be useful to make a rough preliminary investigation of the regions in which we shall have to look for cases of limiting stability in the two problems. For this purpose I consider the case of two spheres as the analogue of the problem of the figure of equilibrium, and the case of a sphere and a particle as the analogue of ROCHE's problem.

Let ρ be density, and let the mass of the whole system be $\frac{4}{3}\pi\rho a^3$; let the masses ot the two spheres be $\frac{4}{3}\pi\rho a^3\lambda/(1+\lambda)$ and $\frac{4}{3}\pi\rho a^3/(1+\lambda)$, or for ROCHE's problem let the latter be the mass of the particle.

Let r be the distance from the centre of one sphere to that of the other, or to the particle, as the case may be; and ω the orbital angular velocity.

In both cases we have

$$\omega^2 r^3 = \tfrac{4}{3}\pi\rho a^3.$$

The centre of inertia of the two masses is distant $r/(1+\lambda)$ and $\lambda r/(1+\lambda)$ from their respective centres, and we easily find the orbital momentum to be

$$\tfrac{4}{3}\pi\rho a^3 \omega r^2 \frac{\lambda}{(1+\lambda)^2}.$$

In both problems the rotational momentum of the first sphere is

$$\tfrac{2}{5}\left(\tfrac{4}{3}\pi\rho \mathrm{a}^3\right)\mathrm{a}^2\left(\frac{\lambda}{1+\lambda}\right)^{5/3}\omega.$$

In the first problem the rotational momentum of the second sphere is

$$\tfrac{2}{5}\left(\tfrac{4}{3}\pi\rho \mathrm{a}^3\right)\mathrm{a}^2\frac{1}{(1+\lambda)^{5/3}}\omega,$$

and in the second problem it is nil.

If, then, we write L_1 for the total angular momentum of the two spheres, and L_2 for that of the sphere and particle, we have

$$\left.\begin{aligned} L_1 &= \tfrac{4}{3}\pi\rho \mathrm{a}^5\omega\left[\tfrac{2}{5}\frac{1+\lambda^{5/3}}{(1+\lambda)^{5/3}}+\frac{\lambda r^2}{(1+\lambda)^2\mathrm{a}^2}\right], \\ L_2 &= \tfrac{4}{3}\pi\rho \mathrm{a}^5\omega\left[\tfrac{2}{5}\frac{\lambda^{5/3}}{(1+\lambda)^{5/3}}+\frac{\lambda r^2}{(1+\lambda)^2\mathrm{a}^2}\right]. \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

On substituting for ω its value in terms of r, these expressions become

$$L_1 = \left(\tfrac{4}{3}\pi\rho\right)^{3/2}\frac{\mathrm{a}^5}{(1+\lambda)^2}\left[\tfrac{2}{5}(1+\lambda^{5/3})(1+\lambda)^{1/3}\left(\frac{\mathrm{a}}{r}\right)^{3/2}+\lambda\left(\frac{r}{\mathrm{a}}\right)^{1/2}\right],$$

$$L_2 = \left(\tfrac{4}{3}\pi\rho\right)^{3/2}\frac{\mathrm{a}^5}{(1+\lambda)^2}\left[\tfrac{2}{5}\lambda^{5/3}(1+\lambda)^{1/3}\left(\frac{\mathrm{a}}{r}\right)^{3/2}+\lambda\left(\frac{r}{\mathrm{a}}\right)^{1/2}\right].$$

To determine the minima of these functions, we differentiate with respect to r, and equate to zero.

Then, if r_1, r_2 denote the two solutions, we find

$$\left(\frac{r_1}{\mathrm{a}}\right)^2 = \frac{6}{5\lambda}(1+\lambda^{5/3})(1+\lambda)^{1/3},$$

$$\left(\frac{r_2}{\mathrm{a}}\right)^2 = \tfrac{6}{5}\lambda^{2/3}(1+\lambda)^{1/3}.$$

Whence

$$\text{Minimum } L_1 = \left(\tfrac{4}{3}\pi\rho\right)^{3/2}\mathrm{a}^5 \,.\, 4\left(\tfrac{2}{135}\right)^{1/4}\frac{\lambda^{3/4}(1+\lambda^{5/3})^{1/4}}{(1+\lambda)^{23/12}},$$

$$\text{Minimum } L_2 = \left(\tfrac{4}{3}\pi\rho\right)^{3/2}\mathrm{a}^5 \,.\, 4\left(\tfrac{2}{135}\right)^{1/4}\frac{\lambda^{7/6}}{(1+\lambda)^{23/12}}.$$

The ratio of the minimum of L_1 to that of L_2 is $\left(\frac{1}{\lambda^{5/3}}+1\right)^{1/4}$. Thus as λ rises from 0 to ∞ this ratio falls from infinity to unity.

All the possible cases of the first problem are comprised between $\lambda = 0$ and $\lambda = 1$. When $\lambda = 0$, $r_1 = \infty$; and when $\lambda = 1$,

$$\frac{r_1}{\mathrm{a}} = \sqrt{\left(\tfrac{12}{5}\,.\,2^{1/3}\right)} = 1{\cdot}738.$$

Thus, in the problem of the figures of equilibrium, if one of the two masses is large compared with the other, the two must be far apart to secure secular stability. This is exactly what is to be expected from the theory of tidal friction, for limiting stability is reached when there is coalescence of the two solutions which correspond to the cases where each body always presents the same face to the other.*

The result when the two masses are equal becomes more easily intelligible when it is expressed in terms of the radius of either of them. That radius is $a/2^{1/3}$, so that when $\lambda = 1$

$$r = 1{\cdot}738a = 2{\cdot}191\left(\frac{a}{2^{1/3}}\right).$$

Thus, in the latter case, limiting stability is reached when the two spheres are nearly in contact with one another, for if r were equal to twice the radius of either they would be touching.

When the two bodies are far apart, the solution may be obtained by spherical harmonic analysis, and has comparatively little interest. But when the bodies are equal or nearly equal in mass, limiting stability for the figure of equilibrium would seem, from this preliminary investigation, to occur when they are quite close together. Accordingly, in finding numerical solutions hereafter, I have devoted more attention to this case than to any other.

Turning now to the solution of the analogue of ROCHE'S problem, we see that when $\lambda = 0$, $r_2 = 0$. This would mean that a very small liquid satellite could be brought quite up to its planet without becoming unstable. But we shall see that, when the satellite is no longer constrainedly a sphere, instability first occurs through the variations in the shape of the satellite. This preliminary solution does not, therefore, throw much light on the matter, excepting as indicating that we must consider the cases where the satellite is as near to the planet as possible.

Next, when $\lambda = 1$, we have

$$r_2 = \sqrt{\left(\tfrac{6}{5} \cdot 2^{1/3}\right)}\, a = \sqrt{\tfrac{12}{5}} \cdot \left(\frac{a}{2^{1/3}}\right) = 1{\cdot}549\left(\frac{a}{2^{1/3}}\right).$$

Thus, when the two masses are equal, their distance apart is only about $1\frac{1}{2}$ radii of either, and they will overlap. Here again it would seem as if stability would persist up to contact, but, as before, instability first sets in through variations in the shape of the satellite.

Finally, when λ is large, r_2 also becomes large. This case is the same in principle as that considered in the problem of the figures of equilibrium, for it means that if a large liquid body (formerly called the satellite) be attended by a small rigid body (formerly called the planet), secular stability will be attained when the small rigid body has been repelled by tidal friction to a great distance from the large liquid body.

---

* See 'Roy. Soc. Proc.,' vol. 29, 1879, p. 168, or Appendix G (*b*) to THOMSON and TAIT'S 'Nat. Phil.'

As this case may be adequately treated by spherical harmonic analysis, it need not detain us, and we see that the most interesting cases of ROCHE's problem are those where λ lies between 0 and 1.

§ 2. *Figures of Equilibrium of a Rotating Mass of Liquid and their Stability.*

A mass of liquid, consisting of either one or more portions, is rotating, without relative motion of its parts, about an axis through its centre of inertia with angular velocity ω. We choose as an arbitrary standard figure one which does not differ very widely from a figure of equilibrium, and we suppose that any departure from the standard figure may be defined by two parameters e and f, which may be called ellipticities. It is unnecessary to introduce more than two ellipticities, because the result for any number becomes obvious from the case of two. We also assume a definite angular velocity for the standard configuration.

Let $V(e, f)$ denote the gravitational energy lost in the concentration of the system from a condition of infinite dispersion into the configuration denoted by e, f.

Let $I(e, f)$, $\omega(e, f)$ denote the moment of inertia and angular velocity about the axis of rotation in the same configuration.

The initial values of these quantities are those for which $e = f = 0$, and are $V(0, 0)$, $I(0, 0)$, $\omega(0, 0)$. These all refer to the arbitrary standard configuration; they are therefore constants, and I shall write them V, I, ω for brevity.

Let ellipticities e, f be imparted to the system, and let the angular velocity be so changed that the angular momentum remains constant.

Then

$$I(e, f)\,\omega(e, f) = I(0, 0)\,\omega(0, 0) = I\omega.$$

The kinetic energy of the system is half the square of the angular momentum divided by the moment of inertia; and since the angular momentum is constant it is equal to $\frac{1}{2}(I\omega)^2/I(e, f)$.

Thus the whole energy of the system, both kinetic and potential, is equal to

$$-V(e, f) + \frac{\frac{1}{2}(I\omega)^2}{I(e, f)}.$$

If $V(e, f) = V + \delta V$, $I(e, f) = I + \delta I$, the expression for the energy as far as squares of small quantities is

$$-(V + \delta V) + \frac{\frac{1}{2}(I\omega)^2}{I + \delta I} = -V + \tfrac{1}{2}I\omega^2 - \delta V - \tfrac{1}{2}\omega^2\delta I + \tfrac{1}{2}\omega^2\frac{(\delta I)^2}{I}.$$

The first two terms may be omitted as being constant and of no interest, and the energy with the sign changed, so that it is the lost energy of the system, becomes

$$\delta V + \tfrac{1}{2}\omega^2\delta I - \tfrac{1}{2}\omega^2\frac{(\delta I)^2}{I}.$$

Since ω is constant, we may write this

$$\delta\left(V+\tfrac{1}{2}\omega^2 I\right)-\tfrac{1}{2}\omega^2\frac{(\delta I)^2}{I}.$$

On developing this by TAYLOR's theorem, it becomes

$$\left(e\frac{\partial}{\partial e}+f\frac{\partial}{\partial f}+\tfrac{1}{2}e^2\frac{\partial^2}{\partial e^2}+ef\frac{\partial^2}{\partial e\partial f}+\tfrac{1}{2}f^2\frac{\partial^2}{\partial f^2}\right)\left(V+\tfrac{1}{2}\omega^2 I\right)-\tfrac{1}{2}\frac{\omega^2}{I}\left(e\frac{\partial I}{\partial e}+f\frac{\partial I}{\partial f}\right)^2.$$

The condition for a figure of equilibrium is that the first differentials of the energy with respect to the ellipticities shall vanish. If, therefore, e_0, f_0 denote the equilibrium ellipticities, the equations for finding them are

$$\left(\frac{\partial}{\partial e}+e_0\frac{\partial^2}{\partial e^2}+f_0\frac{\partial^2}{\partial e\partial f}\right)\left(V+\tfrac{1}{2}\omega^2 I\right)-\frac{\omega^2}{I}\left[e_0\left(\frac{\partial I}{\partial e}\right)^2+f_0\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}\right]=0,$$

$$\left(\frac{\partial}{\partial f}+e_0\frac{\partial^2}{\partial e\partial f}+f_0\frac{\partial^2}{\partial f^2}\right)\left(V+\tfrac{1}{2}\omega^2 I\right)-\frac{\omega^2}{I}\left[e_0\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}+f_0\left(\frac{\partial I}{\partial f}\right)^2\right]=0.$$

Multiplying the first of these by e and the second by f, and adding them together, we find

$$\left(e\frac{\partial}{\partial e}+f\frac{\partial}{\partial f}\right)\left(V+\tfrac{1}{2}\omega^2 I\right)=-\left[ee_0\frac{\partial^2}{\partial e^2}+(ef_0+e_0f)\frac{\partial^2}{\partial e\partial f}+ff_0\frac{\partial^2}{\partial f^2}\right]\left(V+\tfrac{1}{2}\omega^2 I\right)$$
$$+\frac{\omega^2}{I}\left[ee_0\left(\frac{\partial I}{\partial e}\right)^2+(ef_0+e_0f)\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}+ff_0\left(\frac{\partial I}{\partial f}\right)^2\right].$$

On substituting this in the expression for the lost energy, it becomes

$$\left[\tfrac{1}{2}e(e-2e_0)\frac{\partial^2}{\partial e^2}+(ef-ef_0-e_0f)\frac{\partial^2}{\partial e\partial f}+\tfrac{1}{2}f(f-2f_0)\frac{\partial^2}{\partial f^2}\right]\left(V+\tfrac{1}{2}\omega^2 I\right)$$
$$-\tfrac{1}{2}\frac{\omega^2}{I}\left[e(e-2e_0)\left(\frac{\partial I}{\partial e}\right)^2+2(ef-ef_0-e_0f)\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}+f(f-2f_0)\left(\frac{\partial I}{\partial f}\right)^2\right].$$

Now let δe, δf be the excesses of e and f above their equilibrium values e_0, f_0, so that $e=e_0+\delta e$, $f=f_0+\delta f$. Then on substitution in the expression for the lost energy it becomes

$$\left[\tfrac{1}{2}\{(\delta e)^2-e_0^2\}\frac{\partial^2}{\partial e^2}+\{\delta e\delta f-e_0f_0\}\frac{\partial^2}{\partial e\partial f}+\tfrac{1}{2}\{(\delta f)^2-f_0^2\}\frac{\partial^2}{\partial f^2}\right]\left(V+\tfrac{1}{2}\omega^2 I\right)$$
$$-\tfrac{1}{2}\frac{\omega^2}{I}\left[\{(\delta e)^2-e_0^2\}\left(\frac{\partial I}{\partial e}\right)^2+2\{\delta e\delta f-e_0f_0\}\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}+\{(\delta f)^2-f_0^2\}\left(\frac{\partial I}{\partial f}\right)^2\right].$$

Since e_0, f_0 are constants, the portion of this involving e_0, f_0 explicitly is constant, and may be dropped.

Thus the variable part of the lost energy may be written

$$\tfrac{1}{2}(\delta e)^2\left[\frac{\partial^2 V}{\partial e^2}+\tfrac{1}{2}\omega^2\left(\frac{\partial^2 I}{\partial e^2}-\frac{2}{I}\left(\frac{\partial I}{\partial e}\right)^2\right)\right]+\delta e\delta f\left[\frac{\partial^2 V}{\partial e\partial f}+\tfrac{1}{2}\omega^2\left(\frac{\partial^2 I}{\partial e\partial f}-\frac{2}{I}\frac{\partial I}{\partial e}\frac{\partial I}{\partial f}\right)\right]$$

$$+\tfrac{1}{2}(\delta f)^2\left[\frac{\partial^2 V}{\partial f^2}+\tfrac{1}{2}\omega^2\left(\frac{\partial^2 I}{\partial f^2}-\frac{2}{I}\left(\frac{\partial I}{\partial f}\right)^2\right)\right].$$

This is a quadratic function of the departures of the ellipticities from their equilibrium values, and the form is obvious which the result would have if there were any number of ellipticities.

Since the condition for secular stability is that the energy shall be a minimum, the lost energy must be a maximum, and therefore this quadratic function of δe, δf, &c., must always be negative in order that the system may possess secular stability.*

If F is a quadratic function of n variables, x_1, x_2, x_3, &c., so that

$$\begin{aligned}F = a_{11}x_1^2&+2a_{12}.x_1x_2+2a_{13}x_1x_3+\ldots\\ &+\ a_{22}x_2^2\quad+2a_{23}x_2x_3+\ldots\\ &\qquad\qquad\quad+\ a_{33}x_3^2\ +\ldots,\end{aligned}$$

it is known that the condition that F shall always be negative for all values of the variables is that the series of functions

$$a_{11}\,,\quad \begin{vmatrix} a_{11}, & a_{12} \\ a_{12}, & a_{22}\end{vmatrix}\,,\quad \begin{vmatrix} a_{11}, & a_{12}, & a_{13} \\ a_{12}, & a_{22}, & a_{23} \\ a_{13}, & a_{23}, & a_{33}\end{vmatrix}\,,\ \ldots \qquad (2)$$

shall be alternatively negative and positive.

Since we might equally well begin with any one of the variables, it follows that a_{11}, a_{22}, $a_{33}\ldots$ must all be negative; also $a_{12}^2-a_{11}a_{22}$, $a_{13}^2-a_{11}a_{33}$, $a_{23}^2-a_{22}a_{33}\ldots$ must all be negative if F is always to be negative.

Now, suppose that F is the function of lost energy for a system with $n+1$ degrees of freedom, but that a constraint destroys one of the degrees. If the system has secular stability, the n determinants must have their appropriate signs, and when the constraint is removed, the new additional determinant must have its proper sign in order to secure secular stability. It follows that stability can never be restored by the removal of a constraint if the system was unstable when the constraint existed; but stability may be destroyed by the removal of a constraint.

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* This result is also given, but with less detail, in my paper on "MACLAURIN'S Spheroid," in 'Trans. Amer. Math. Soc.,' vol. 4, No. 2, pp. 113–133 (1903).

§ 3. *On the Possibility of joining Two Masses of Liquid by a thin Neck.*

This whole investigation was undertaken principally in the hope that it might lead to an approximation to the form of the pear-shaped figure of equilibrium of a rotating mass of liquid at the stage when it should resemble an hour-glass with a thin neck. It seemed probable that such an approximation might be obtained in the following manner :—

Two masses of liquid are revolving in an orbit about one another without relative motion of their parts, so that they form a figure of equilibrium. Imagine them to be joined by a pipe without weight, through which liquid may flow from one part to the other. A flow of liquid will in general take place between the two parts, but there should be some definite partition of masses, corresponding to a given distance apart, at which flow will cease. At this stage we should have an approximation to the hour-glass figure of equilibrium.

In this section a special case of this problem is considered, in which the detached masses, to be joined by a pipe, are constrained to be spheres.

If the notation of § 1 be adopted, it is clear that the system is defined by the two parameters r and λ. In accordance with the notation of § 2 we denote the lost energy of the system by V and the moment of inertia by I. It is easily shown that

$$V = (\tfrac{4}{3}\pi\rho)^2 \mathrm{a}^5 \left[\frac{\lambda}{(1+\lambda)^2}\frac{\mathrm{a}}{r} + \tfrac{3}{5}\frac{1+\lambda^{5/3}}{(1+\lambda)^{5/3}}\right],$$

$$I = \tfrac{4}{3}\pi\rho\mathrm{a}^5 \left[\frac{\lambda}{(1+\lambda)^2}\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}\frac{1+\lambda^{5/3}}{(1+\lambda)^{5/3}}\right].$$

For brevity write

$$F = \frac{\lambda}{(1+\lambda)^2}, \quad G = \frac{1+\lambda^{5/3}}{(1+\lambda)^{5/3}},$$

and let F', G', F'', G'' denote their first and second differentials with respect to λ.

The equations for determining the configuration of equilibrium are

$$\frac{\partial V}{\partial r} + \tfrac{1}{2}\omega^2\frac{\partial I}{\partial r} = 0, \quad \frac{\partial V}{\partial \lambda} + \tfrac{1}{2}\omega^2\frac{\partial I}{\partial \lambda} = 0.$$

The first of these gives at once

$$\omega^2 = \tfrac{4}{3}\pi\rho\left(\frac{\mathrm{a}}{r}\right)^3.$$

For determining the form of the second we have

$$V = (\tfrac{4}{3}\pi\rho)^2\mathrm{a}^5\left[F\frac{\mathrm{a}}{r} + \tfrac{3}{5}G\right], \quad I = \tfrac{4}{3}\pi\rho\mathrm{a}^5\left[F\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G\right].$$

If we differentiate these with respect to λ, substitute in the second equation of equilibrium and give to ω^2 its value in terms of r^2, we find that the result is

$$\frac{\mathrm{a}^3}{r^3}+\tfrac{15}{2}\frac{F'}{G'}\frac{\mathrm{a}}{r}+3=0.$$

Now

$$F'=\frac{1-\lambda}{(1+\lambda)^3},\quad G'=\tfrac{5}{3}\frac{\lambda^{2/3}-1}{(1+\lambda)^{8/3}},\quad \text{and}\quad \frac{F'}{G'}=-\tfrac{3}{5}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}.$$

Hence the equation for determining r for a given value of λ is

$$\frac{\mathrm{a}^3}{r^3}-\tfrac{9}{2}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}\frac{\mathrm{a}}{r}+3=0 \quad \ldots\ldots\ldots \quad (3).$$

This cubic has three real roots of which one is negative and has no physical meaning; the second gives so small a value to r that the smaller sphere is either wholly or partially inside the larger one. The third root is the one required.

In order to present the result in an easily intelligible form it may be well to express it also in terms of the radius of the larger of the two spheres, say a_1, where

$$\mathrm{a}_1{}^3=\frac{\mathrm{a}^3}{1+\lambda}.$$

The following is a table of solutions for various values of λ :—

$\lambda^{1/3}$.	r/a.	r/a_1.	$r/\mathrm{a}_1-(1+\lambda^{1/3})$.
0·0	1·304	1·304	0·304
0·1	1·323	1·323	0·223
0·2	1·368	1·371	0·171
0·3	1·426	1·438	0·138
0·4	1·486	1·517	0·117
0·5	1·543	1·604	0·104
0·6	1·590	1·697	0·097
0·7	1·625	1·793	0·093
0·8	1·649	1·893	0·093
0·9	1·662	1·995	0·095
1·0	1·666	2·099	0·099

The solution is exhibited in fig. 1, the larger sphere being kept of constant size and the successive smaller circles representing the smaller sphere. Many of the circles pass nearly through one point, and it has not been possible to complete them without producing confusion.

The fourth column of the table gives the excess of r above the sum of the two radii of the spheres, and it shows what interval of space is unoccupied by matter. It is remarkable how nearly constant that interval is throughout a large range in the values of λ.

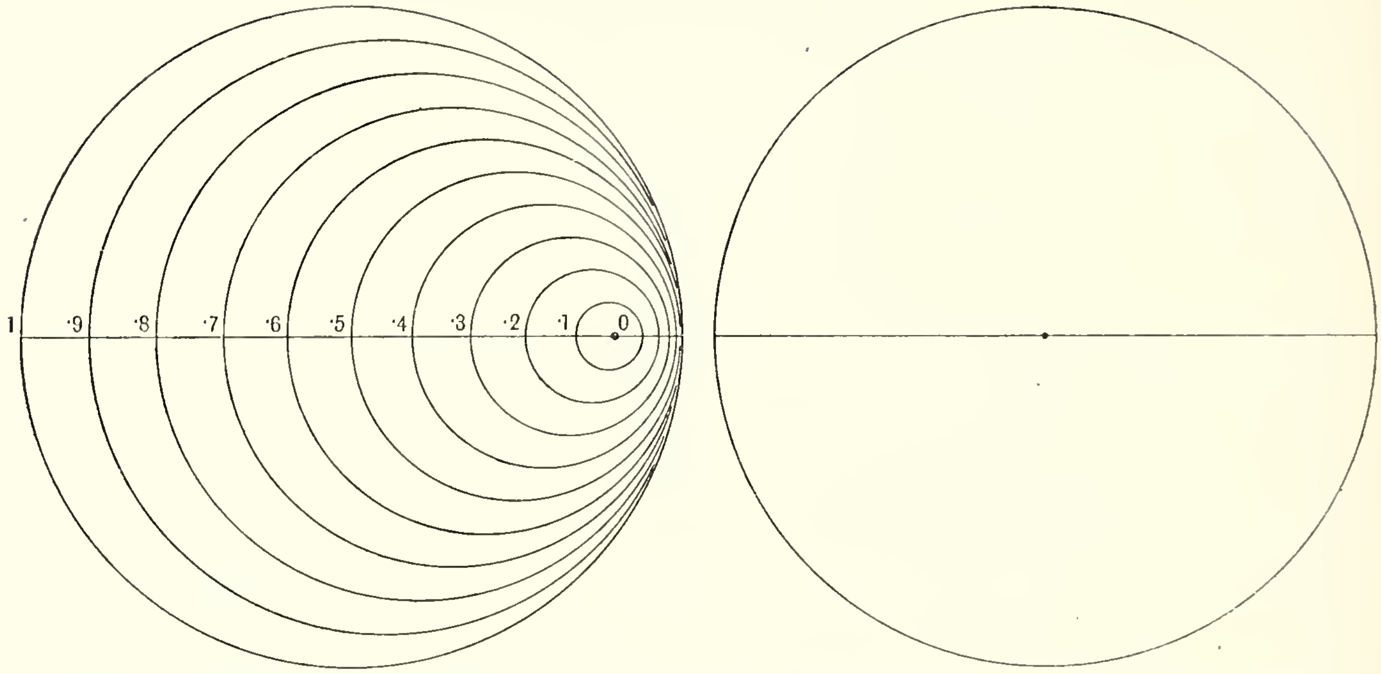

Fig. 1. Solutions for two spheres of liquid joined by a weightless pipe, for successive values of $\lambda^{1/3}$.

In the case where the two bodies are no longer spheres, the equation corresponding to the cubic (3) becomes very complicated. It is therefore desirable to discover whether in any given solution of the figure of equilibrium the two detached masses are too far apart to admit of their being joined by a weightless pipe, or whether they are too near. This may be discovered in the following way :—

Let r_0 be the solution of $f(\mathrm{a}/r_0) = 0$, where

$$f\left(\frac{\mathrm{a}}{r}\right) = \frac{\mathrm{a}^3}{r^3} - \frac{9}{2}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}\frac{\mathrm{a}}{r} + 3. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

There is only one solution of $f = 0$ between r equal to infinity and the case when the two spheres touch. Hence we can determine on which side of r_0 any given value of r lies by merely considering whether f changes from positive to negative or from negative to positive as r increases through the value r_0.

Now if $\frac{\mathrm{a}}{r_0} + \delta\left(\frac{\mathrm{a}}{r}\right)$ be any neighbouring value of $\frac{\mathrm{a}}{r}$, we have approximately

$$f\left(\frac{\mathrm{a}}{r}\right) = 3\left[\frac{\mathrm{a}^2}{r_0^{\,2}} - \frac{3}{2}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}\right]\delta\left(\frac{\mathrm{a}}{r}\right).$$

If we express $\mathrm{a}^2/r_0^{\,2}$ in terms of r_0/a by means of the equation for r_0, this may be written

$$f\left(\frac{\mathrm{a}}{r}\right) = \frac{9}{(1+\lambda)^{1/3}}\left(1+\lambda^{1/3} - \frac{r}{\mathrm{a}_1} - \frac{\lambda^{1/3}}{1+\lambda^{1/3}}\right)\delta\left(\frac{\mathrm{a}}{r}\right),$$

where as before

$$\mathrm{a}_1^{\,3} = \frac{\mathrm{a}^3}{1+\lambda}.$$

Now the fourth column of the table shows that $1+\lambda^{1/3}-r/\mathrm{a}_1$ is negative, and the last term inside the bracket is also negative. Hence if $\delta\left(\frac{\mathrm{a}}{r}\right)$ is negative, $f\left(\frac{\mathrm{a}}{r}\right)$ is positive, and *vice versâ*. But if $\delta\left(\frac{\mathrm{a}}{r}\right)$ is negative, r is greater than r_0 and the two masses are too far apart to admit of junction, and *vice versâ*.

Therefore if for a given solution for detached masses $f\left(\frac{\mathrm{a}}{r}\right)$ is positive, the masses are too far apart to admit of junction by a weightless pipe, and if it is negative they are too near.

When in the general case we form a function $f(\mathrm{a}/r)$, such that when the ellipticities of the two masses are annulled, it reduces to the above function, its sign will afford the criterion as to whether the masses are too far or too near to admit of junction by a thin neck of liquid. I return to this subject below in § 13.

The solution of the problem when the two masses are constrainedly spheres is so curious that it seems worth while to consider its stability. This may be done by the method of § 2.

The system depends on two parameters r and λ, and the stability will depend on three functions, which are defined as follows:—

$$\{r, r\} = \frac{\partial^2 V}{\partial r^2} + \tfrac{1}{2}\omega^2 \frac{\partial^2 I}{\partial r^2} - \frac{\omega^2}{I}\left(\frac{\partial I}{\partial r}\right)^2,$$

$$\{r, \lambda\} = \frac{\partial^2 V}{\partial r \partial \lambda} + \tfrac{1}{2}\omega^2 \frac{\partial^2 I}{\partial r \partial \lambda} - \frac{\omega^2}{I}\frac{\partial I}{\partial r}\frac{\partial I}{\partial \lambda},$$

$$\{\lambda, \lambda\} = \frac{\partial^2 V}{\partial \lambda^2} + \tfrac{1}{2}\omega^2 \frac{\partial^2 I}{\partial \lambda^2} - \frac{\omega^2}{I}\left(\frac{\partial I}{\partial \lambda}\right)^2.$$

These functions correspond to a_{11}, a_{12}, a_{22} of (2) in § 2, and we see that for secular stability $\{r, r\}$ and $\{\lambda, \lambda\}$ must be negative, and

$$\Delta = \{r, r\}\{\lambda, \lambda\} - [\{r, \lambda\}]^2$$

must be positive.

Without giving the details of the several differentiations, I may state that if we write

$$H = (\tfrac{4}{3}\pi\rho)^2 \mathrm{a}^3 \cdot \frac{F\dfrac{\mathrm{a}^3}{r^3}}{F\dfrac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G},$$

so that H is essentially positive, we find

$$\frac{\{r, r\}}{H} = \tfrac{6}{5}G - F\frac{r^2}{\mathrm{a}^2}; \qquad \frac{\{r, \lambda\}}{H} = -2r\left(F'\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G'\right);$$

$$\frac{\{\lambda, \lambda\}}{H} = \frac{\mathrm{a}^2}{F}\left\{\left[\tfrac{3}{2}F''\frac{r^2}{\mathrm{a}^2} + \tfrac{1}{5}G''\left(1 + 3\frac{r^3}{\mathrm{a}^3}\right)\right]\left[F\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G\right] - \left[F'\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G'\right]^2\right\}.$$

From the equation

$$\frac{\mathrm{a}^3}{r^3} + \tfrac{15}{2}\frac{F'}{G'}\frac{\mathrm{a}}{r} + 3 = 0,$$

we find, after some reductions,

$$\tfrac{3}{2}F''\frac{r^2}{\mathrm{a}^2} + \tfrac{1}{5}G''\left(1 + 3\frac{r^3}{\mathrm{a}^3}\right) = \tfrac{3}{2}\frac{r^2}{\mathrm{a}^2}F'\frac{d}{d\lambda}\log\frac{F'}{G'}.$$

On substituting for F', G' their values in terms of λ, I find that this expression reduces to

$$\frac{(1-\lambda^{1/3})^2}{\lambda^{1/3}(1+\lambda)^4}\frac{r^2}{\mathrm{a}^2},$$

an essentially positive quantity.

On substitution in Δ I find

$$\Delta = \frac{H^2\mathrm{a}^2}{F}\left(F\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G\right)\left[\frac{(1-\lambda^{1/3})^2}{\lambda^{1/3}(1+\lambda)^4}\frac{r^2}{\mathrm{a}^2}\left(\tfrac{6}{5}G - F\frac{r^2}{\mathrm{a}^2}\right) - 3\left(F'\frac{r^2}{\mathrm{a}^2} + \tfrac{2}{5}G'\right)^2\right]. \quad . \quad . \quad (5)$$

The factors outside [ ] are essentially positive and do not affect the sign of Δ, and it is clear that Δ can only be positive if $\tfrac{6}{5}G - F\frac{r^2}{\mathrm{a}^2}$ is positive. But Δ must be positive for secular stability; hence stability can only be secured by $\tfrac{6}{5}G - F\frac{r^2}{\mathrm{a}^2}$ being positive, and it is not necessarily so secured. But if this function is positive, so also is $\{r, r\}$, and if this last is positive the system is unstable. Hence stability is always impossible. As a fact, in all the solutions given above $\{r, r\}$ is positive, and we should have to move the spheres much further apart to make it negative, and therefore on this ground alone the system is always unstable. But Δ is sometimes positive and sometimes negative and vanishes for a certain value of λ. As the vanishing of Δ puzzled me a good deal, I propose to examine the matter further.

Before doing so, however, I will show that the instability of the system may be concluded from other considerations.

It was proved in § 1 that two spheres, unconnected by a pipe, are in limiting stability when their distance apart is given by

$$\frac{r^2}{\mathrm{a}^2} = \frac{6}{5\lambda}(1+\lambda^{5/3})(1+\lambda)^{1/3} = \tfrac{6}{5}\frac{G}{F}.$$

This is the condition that $\{r, r\}$ should vanish.

When λ is zero the two spheres in limiting stability are infinitely far apart, and when λ is unity they are as near as possible, and $r = 1{\cdot}738\mathrm{a}$.

Now the table of solutions in the case where the two are connected by a pipe shows that they are furthest apart when λ is unity, and that then $r = 1{\cdot}666\mathrm{a}$.

The removal of the constraint of one degree of freedom may destroy stability, but cannot create it. Hence, when two spheres revolve about one another, the opening of a channel of communication between them may destroy stability, but cannot create it. When two equal spheres revolve about one another at such a distance that they could be connected by a pipe and yet remain in equilibrium, their distance is 1·666; but they are then unstable, because 1·666 is less than 1·738. The opening of a pipe between them, being the removal of a constraint, cannot make the motion stable. *À fortiori* the like is true when the two spheres are unequal in mass.

Hence the system of equilibrium of two spheres joined by a pipe is unstable in all cases.

I will now consider the meaning of the vanishing of Δ.

Having evaluated the angular momentum of the system corresponding to the several solutions tabulated above, I found it had a minimum when $\lambda^{1/3} = 0{\cdot}254$. Such a solution is a critical one and is the starting point of two solutions of which one must have one fewer degrees of instability than the other. The vanishing of Δ must have the same meaning, but it remains to be proved that minimum angular momentum is secured by the vanishing of Δ.

The angular momentum is $I\omega$, and is therefore proportional to μ, where

$$\mu = F\left(\frac{r}{a}\right)^{1/2} + \tfrac{2}{5}G\left(\frac{a}{r}\right)^{3/2}.$$

On equating $\dfrac{d\mu}{d\lambda}$ to zero so as to find its minimum, we have

$$2r\left(F'\frac{r^2}{a^2} + \tfrac{2}{5}G'\right) + \left(F\frac{r^2}{a^2} - \tfrac{6}{5}G\right)\frac{dr}{d\lambda} = 0.$$

Now since

$$\frac{r^3}{a^3} + \tfrac{1}{3} + \tfrac{5}{2}\frac{F'}{G'}\frac{r}{a} = 0,$$

we have

$$\frac{dr}{d\lambda} = \frac{-\tfrac{1}{3}r\,(1-\lambda^{1/3})^2\,\lambda^{-1/3}\,(1+\lambda)^{-4}}{\tfrac{3}{5}G'\dfrac{r}{a} + F'}.$$

On substituting this value in the equation $d\mu/d\lambda = 0$, I find that the result may be written

$$\frac{(1-\lambda^{1/3})^2}{\lambda^{1/3}\,(1+\lambda)^4}\,\frac{r^2}{a^2}\left(\tfrac{6}{5}G - F\frac{r^2}{a^2}\right) + 6\,\frac{r^2}{a^2}\left(F'\frac{r^2}{a^2} + \tfrac{2}{5}G'\right)\left(\tfrac{3}{5}G'\frac{r}{a} + F'\right) = 0.$$

The first term of this is the same as the first term inside the bracket in the expression for Δ in (5). On comparing the two second terms together we see that $\Delta = 0$ is the condition for minimum angular momentum, if

$$6\,\frac{r^2}{a^2}\left(F'\frac{r^2}{a^2} + \tfrac{2}{5}G'\right)\left(\tfrac{3}{5}G'\frac{r}{a} + F'\right) = -3\left(F'\frac{r^2}{a^2} + \tfrac{2}{5}G'\right)^2;$$

that is to say, if

$$2\frac{r^2}{\mathrm{a}^2}\left(\tfrac{3}{5}G'\frac{r}{\mathrm{a}}+F'\right)+F'\frac{r^2}{\mathrm{a}^2}+\tfrac{2}{5}G'=0,$$

or if

$$\frac{\mathrm{a}^3}{r^3}+\tfrac{15}{2}\frac{F'}{G'}\frac{\mathrm{a}}{r}+3=0.$$

But this last is true, being the equation (3) determining the figure of equilibrium; hence $\Delta = 0$ gives minimum angular momentum.

Since two liquid spheres cannot be joined stably by a pipe, it seems very improbable that two tidal ellipsoids could be so joined as to become stable. Indeed, if the distortion of the surfaces of the two masses into ellipsoidal forms may be regarded as due to the removal of constraints whereby they were previously maintained in a spherical form, stability is impossible.

The question as to whether or not there is an unstable figure with a thin neck will be considered later, for the present we are only concerned with the conclusion that there is no stable figure of this kind.

Mr. JEANS has treated an analogous problem in his paper on the equilibrium of rotating liquid cylinders,* and has concluded that the cylinder will divide stably into two portions. The analogy is so close between his problem and the three-dimensional case, that it might have been expected that the analogy would subsist throughout; nevertheless, if we are both correct there must be a divergence between them at some point.

§ 4. *Notation.*

As the solution given below is effected by means of ellipsoidal harmonic analysis, it is well to state the notation employed. It is that used in four previous papers to which references are given in the Preface.

In "Harmonics" the squares of the semi-axes of the ellipsoid were

$$a^2=k^2\left(\nu^2-\frac{1+\beta}{1-\beta}\right),\quad b^2=k^2(\nu^2-1),\quad c^2=k^2\nu^2.$$

The rectangular co-ordinates were connected with ellipsoidal co-ordinates ν, μ, ϕ by

$$\frac{x^2}{k^2}=-\frac{1-\beta}{1+\beta}\left(\nu^2-\frac{1+\beta}{1-\beta}\right)\left(\mu^2-\frac{1+\beta}{1-\beta}\right)\cos^2\phi,$$

$$\frac{y^2}{k^2}=-(\nu^2-1)(\mu^2-1)\sin^2\phi,$$

$$\frac{z^2}{k^2}=\nu^2\mu^2\frac{1-\beta\cos 2\phi}{1+\beta}.$$

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* 'Phil. Trans. Roy. Soc.,' Series A, vol. 200, pp. 67–104.

The three roots of the cubic

$$\frac{x^2}{a^2+u}+\frac{y^2}{b^2+u}+\frac{z^2}{c^2+u}=1$$

were

$$u_1 = k^2\nu^2, \quad u_2 = k^2\mu^2, \quad u_3 = k^2\frac{1-\beta\cos 2\phi}{1-\beta}.$$

Lastly ν ranges from ∞ to 0, μ between $\pm$ 1, ϕ from 0 to 2π.

In the two later papers, I put

$$\kappa^2 = \frac{1-\beta}{1+\beta}, \quad \kappa'^2 = 1-\kappa^2, \quad \nu = \frac{1}{\kappa\sin\gamma}, \quad \mu = \sin\theta;$$

and for convenience I introduced an auxiliary constant β (easily distinguishable from the β of the previous notation) defined by $\sin\beta = \kappa\sin\gamma$.

The squares of the semi-axes of the ellipsoid were then

$$a^2 = \frac{k^2\cos^2\gamma}{\sin^2\beta}, \quad b^2 = \frac{k^2\cos^2\beta}{\sin^2\beta}, \quad c^2 = \frac{k^2}{\sin^2\beta}.$$

The rectangular co-ordinates became

$$\frac{x^2}{k^2} = \frac{\cos^2\gamma}{\sin^2\beta}(1-\kappa^2\sin^2\theta)\cos^2\phi, \quad \frac{y^2}{k^2} = \frac{\cos^2\beta}{\sin^2\beta}\cos^2\theta\sin^2\phi, \quad \frac{z^2}{k^2} = \frac{1}{\sin^2\beta}\sin^2\theta\,(1-\kappa'^2\cos^2\phi).$$

The roots of the cubic were

$$u_1 = \frac{k^2}{\sin^2\beta}, \quad u_2 = k^2\sin^2\theta, \quad u_3 = \frac{k^2}{\kappa^2}(1-\kappa'^2\cos^2\phi).$$

The notation employed for the harmonic functions is that defined in "Harmonics."

§ 5. *The Determination of Gravity on* ROCHE'S *Ellipsoid.*

In ROCHE'S problem a mass of liquid, which assumes approximately the form of an ellipsoid, revolves in a circular orbit about a distant centre of force without any relative motion. In the present section it is proposed to evaluate gravity on the surface of this ellipsoid. I intend to solve the problems of the present paper by means of the principles of energy, and for that purpose it is necessary to determine the law of gravity.

Suppose that the ellipsoid of reference, defined by ν_0, is deformed by a normal displacement defined by the function $pf(\mu, \phi)$, where p is the perpendicular from the centre on to the tangent plane at μ, ϕ. This deformation must be expressible by a series of ellipsoidal harmonic functions, and therefore we may assume

$$f(\mu, \phi) = \Sigma e_i^s \mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi).$$

The typical term written down must be deemed to include sine-functions as well as cosine-functions, and all those types which I have denoted by **P**, **C**, **S** in "Harmonics."

On multiplying each side of our equation by any harmonic function, and integrating over the surface of the ellipsoid, an element of which surface is denoted by $d\sigma$, we find in the usual way

$$e_i^s = \frac{\int f(\mu, \phi)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)\,p\,d\sigma}{\int [\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma}.$$

Suppose that $f(\mu, \phi)$ is zero everywhere except over a small area $\delta\alpha$ situated at the point μ', ϕ', and that it is there equal to a constant c; also let p' be the value of p at this area $\delta\sigma$.

Then the mass of the inequality is

$$\int \rho f(\mu, \phi)\,p\,d\sigma = cp'\rho\delta\alpha,$$

where ρ is the density of the solid ellipsoid which is deformed.

Next let us suppose that the mass of the inequality is unity, so that

$$cp'\rho\delta\alpha = 1.$$

Then we have

$$\int f(\mu, \phi)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)\,p\,d\sigma = c\mathfrak{P}_i^s(\mu')\,\mathfrak{C}_i^s(\phi')\,p'\delta\alpha = \frac{1}{\rho}\mathfrak{P}_i^s(\mu')\,\mathfrak{C}_i^s(\phi').$$

Hence

$$e_i^s = \frac{\mathfrak{P}_i^s(\mu')\,\mathfrak{C}_i^s(\phi')}{\rho\int [\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma}.$$

I now write M for the mass of the ellipsoid, and shall subsequently make it equal to $\frac{4}{3}\pi\rho a^3\frac{\lambda}{1+\lambda}$, while the mass of the distant particle will be $\frac{M}{\lambda}$ or $\frac{4}{3}\pi\rho a^3\frac{1}{1+\lambda}$.

Since $\int p\rho\,d\sigma = 3M$, and $\mathfrak{P}_0(\mu)\,\mathfrak{C}_0(\phi) = 1$, we have $e_0 = \frac{1}{3M}$.

Thus an inequality representing a particle of unit mass at μ', ϕ' on the surface of the ellipsoid is expressed in ellipsoidal harmonics by

$$p\left[\frac{1}{3M} + \Sigma\frac{\mathfrak{P}_i^s(\mu')\,\mathfrak{C}_i^s(\phi')\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)}{\rho\int [\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma}\right].$$

By the formula (51) of "Harmonics," the external potential at the point ν, μ, ϕ of the inequality is

$$\frac{1}{k}\mathfrak{P}_0(\nu_0)\,\mathfrak{Q}_0(\nu_0) + \frac{3M}{k\rho}\Sigma\frac{\mathfrak{P}_i^s(\mu')\,\mathfrak{C}_i^s(\phi')\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{Q}_i^s(\nu)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)}{\int [\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma}.$$

But if R is the distance between the point ν_0, μ', ϕ' on the ellipsoid and the external point ν, μ, ϕ, this potential is $1/R$.

If we imagine a particle of mass M/λ situated at ν, μ, ϕ, the above expression multiplied by M/λ is the potential of the particle at the point ν_0, μ', ϕ' on the ellipsoid.

We have no need for the general expression for the potential of a particle situated anywhere in space at the surface of the ellipsoid, because it is only necessary to consider the case where the particle lies on the prolongation of the longest axis of the ellipsoid. In this case

$$\mu = 1, \quad \phi = \tfrac{1}{2}\pi, \quad \nu = \frac{r}{k},$$

where r is the distance of the particle from the centre of the ellipsoid.

But it is now no longer necessary to retain the accents to μ', ϕ', since they are only the co-ordinates of a point on the ellipsoid.

Thus the potential of M/λ, lying on the longest axis of the ellipsoid at a distance r from the centre, at the point ν_0, μ, ϕ on the ellipsoid, is

$$\frac{M}{k\lambda}\mathfrak{P}_0(\nu_0)\,\mathfrak{Q}_0\!\left(\frac{r}{k}\right) + \frac{3M^2}{k\lambda\rho}\Sigma\frac{\mathfrak{Q}_i^s\!\left(\frac{r}{k}\right)\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)}{\int[\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma}.$$

For the types of functions denoted in "Harmonics" EES, OOS, OES, EOS, $\mathfrak{P}_i^s(1) = 0$, and for EOC, OOC, $\mathfrak{C}_i^s(\tfrac{1}{2}\pi) = 0$. The only types for which $\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)$ does not vanish are EEC, OEC; that is to say, cosine-functions of even rank. Accordingly the functions left are $\mathfrak{P}_i^s\mathfrak{C}_i^s$ for i and s even, and $\mathfrak{P}_i^s\mathbf{C}_i^s$ for i odd and s even; we may however continue to allow $\mathfrak{C}_i^s$ to stand for both types.

For brevity write

$$\mathfrak{T}_i^s = \frac{(2i+1)\rho}{3M}\int[\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2\,p\,d\sigma.$$

Thence, since $\mathfrak{P}_0(\nu_0) = 1$, the potential may be written

$$\frac{M}{k\lambda}\left\{\mathfrak{Q}_0\!\left(\frac{r}{k}\right) + \sum_1^\infty\frac{2i+1}{\mathfrak{T}_i^s}\mathfrak{Q}_i^s\!\left(\frac{r}{k}\right)\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)\right\} \text{ for all even values of } s.$$

It must be observed that $\mathfrak{P}_i^s$ and $\mathfrak{C}_i^s$ occur as squares in $\mathfrak{T}_i^s$; they also occur twice in the numerator in the forms $\mathfrak{P}_i^s(1)\,\mathfrak{P}_i^s(\mu)$ and $\mathfrak{C}_i^s(\tfrac{1}{2}\pi)\,\mathfrak{C}_i^s(\phi)$.

Again $\mathfrak{Q}_i^s\left(\frac{r}{k}\right)$ is of dimensions -1 in $\mathfrak{P}_i^s$, and therefore $\mathfrak{Q}_i^s\left(\frac{r}{k}\right)\mathfrak{P}_i^s(\nu_0)$ is of zero dimensions. From these considerations it follows that $\mathfrak{P}_i^s(\mu)$ and $\mathfrak{C}_i^s(\phi)$ may be multiplied by any factors without changing the result, and further that $\mathfrak{P}_i^s(\nu)$ may differ in its mode of definition from $\mathfrak{P}_i^s(\mu)$ without producing any change.

The higher harmonics will be considered later, and for the present it is only necessary to consider the terms defined by $i = 1$, $s = 0$ and $i = 2$, $s = 0$ and 2.

The following are the definitions of the several functions, in accordance with "Integrals":—

$$\mathfrak{P}_0(\nu) = 1, \qquad \mathfrak{P}_0(\mu) = 1, \qquad \mathfrak{C}_0(\phi) = 1,$$

$$\mathfrak{P}_1(\nu) = \nu, \qquad \mathfrak{P}_1(\mu) = \mu, \qquad \mathsf{C}_1(\phi) = \sqrt{(1-\kappa'^2\cos^2\phi)},$$

$$\mathfrak{P}_2{}^s(\nu) = \nu^2 - \frac{q_s{}^2}{\kappa^2}, \quad \mathfrak{P}_2{}^s(\mu) = \kappa^2\mu^2 - q_s{}^2, \quad \mathfrak{C}_2{}^s(\phi) = q_s{}'^2 - \kappa'^2\cos^2\phi \quad (s = 0, 2),$$

where $q_s{}^2 = \frac{1}{3}[1+\kappa^2 \mp D]$ and $D^2 = 1-\kappa^2\kappa'^2$, with upper sign for $s = 0$, and lower for $s = 2$.

Hence

$$\mathfrak{P}_1(1)\,\mathfrak{C}_1(\tfrac{1}{2}\pi) = 1, \quad \mathfrak{P}_2{}^s(1)\,\mathfrak{C}_2{}^s(\tfrac{1}{2}\pi) = (\kappa^2 - q_s{}^2)\,q_s{}'^2 \quad (s = 0, 2).$$

Then from "Integrals," equations (5) and (6),

$$\mathfrak{T}_1 = 1, \quad \mathfrak{T}_2{}^s = \frac{2^3}{3^4}[D^4 \pm (1+\tfrac{1}{2}\kappa^2\kappa'^2)(1-2\kappa'^2)\,D] \quad (s = 0, 2).$$

Thus as far as the second order of harmonics the potential of M/λ at ν_0, μ, ϕ is

$$\frac{M}{k\lambda}\left\{\mathfrak{Q}_0\left(\frac{r}{k}\right) + 3\mathfrak{Q}_1\left(\frac{r}{k}\right)\mathfrak{P}_1(\nu_0)\,\mathfrak{P}_1(\mu)\,\mathsf{C}_1(\phi) + \frac{5}{\mathfrak{T}_2}(\kappa^2 - q_0{}^2)\,q_0{}'^2\mathfrak{Q}_2\left(\frac{r}{k}\right)\mathfrak{P}_2(\nu_0)\,\mathfrak{P}_2(\mu)\,\mathfrak{C}_2(\phi)\right.$$
$$\left. + \frac{5}{\mathfrak{T}_2{}^2}(\kappa^2 - q_2{}^2)\,q_2{}'^2\mathfrak{Q}_2{}^2\left(\frac{r}{k}\right)\mathfrak{P}_2{}^2(\nu_0)\,\mathfrak{P}_2{}^2(\mu)\,\mathfrak{C}_2{}^2(\phi)\right\}.$$

We must now express the several solid harmonics involved in this expression in terms of x, y, z co-ordinates of a point on the surface of the ellipsoid.

We have

$$\mathfrak{P}_1(\nu_0)\,\mathfrak{P}_1(\mu)\,\mathsf{C}_1(\phi) = \nu\mu\sqrt{(1-\kappa'^2\cos^2\phi)} = \frac{z}{k}.$$

By the definition of ellipsoidal co-ordinates the three values of ω^2 which satisfy the equation

$$\frac{x^2}{\omega^2 - 1/\kappa^2} + \frac{y^2}{\omega^2 - 1} + \frac{z^2}{\omega^2} - k^2 = 0 \quad \text{are} \quad \nu^2,\ \mu^2,\ \frac{1}{\kappa^2}(1-\kappa'^2\cos^2\phi).$$

Hence we have the following identity

$$\frac{x^2}{\omega^2 - 1/\kappa^2} + \frac{y^2}{\omega^2 - 1} + \frac{z^2}{\omega^2} - k^2 = k^2\frac{(\nu_0{}^2 - \omega^2)(\mu^2 - \omega^2)(1-\kappa'^2\cos^2\phi - \omega^2\kappa^2)}{(\omega^2 - 1/\kappa^2)(\omega^2 - 1)\,\omega^2\kappa^2}.$$

Putting $\omega^2 = \dfrac{q_s{}^2}{\kappa^2}$ $(s = 0, 2)$ we find

$$\mathfrak{P}_2{}^s(\nu_0)\,\mathfrak{P}_2{}^s(\mu)\,\mathfrak{C}_2{}^s(\phi) = q_s{}^2 q_s{}'^2(\kappa^2 - q_s{}^2)\left[-\frac{1}{q_s{}'^2}\cdot\frac{x^2}{k^2} - \frac{1}{\kappa^2 - q_s{}^2}\cdot\frac{y^2}{k^2} + \frac{1}{q_s{}^2}\cdot\frac{z^2}{k^2} - \frac{1}{\kappa^2}\right] (s = 0, 2).$$

Hence the potential of M/λ is

$$
\begin{aligned}
\frac{M}{\lambda k}\Bigg\{ & \mathfrak{Q}_0\left(\frac{r}{k}\right)+3\mathfrak{Q}_1\left(\frac{r}{k}\right)\cdot\frac{z}{k} \\
& +\frac{x^2}{k^2}\left[-\frac{5\mathfrak{Q}_2\left(\frac{r}{k}\right)}{\mathfrak{T}_2}q_0^2q_0'^2(\kappa^2-q_0^2)^2-\frac{5\mathfrak{Q}_2^2\left(\frac{r}{k}\right)}{\mathfrak{T}_2^2}q_2^2q_2'^2(\kappa^2-q_2^2)^2\right] \\
& +\frac{y^2}{k^2}\left[-\frac{5\mathfrak{Q}_2\left(\frac{r}{k}\right)}{\mathfrak{T}_2}q_0^2q_0'^4(\kappa^2-q_0^2)-\frac{5\mathfrak{Q}_2^2\left(\frac{r}{k}\right)}{\mathfrak{T}_2^2}q_2^2q_2'^4(\kappa^2-q_2^2)\right] \\
& +\frac{z^2}{k^2}\left[\frac{5\mathfrak{Q}_2\left(\frac{r}{k}\right)}{\mathfrak{T}_2}q_0'^4(\kappa^2-q_0^2)^2+\frac{5\mathfrak{Q}_2^2\left(\frac{r}{k}\right)}{\mathfrak{T}_2^2}q_2'^4(\kappa^2-q_2^2)^2\right] \\
& -\frac{1}{\kappa^2}\left[\frac{5\mathfrak{Q}_2\left(\frac{r}{k}\right)}{\mathfrak{T}_2}q_0^2q_0'^4(\kappa^2-q_0^2)^2+\frac{5\mathfrak{Q}_2^2\left(\frac{r}{k}\right)}{\mathfrak{T}_2^2}q_2^2q_2'^4(\kappa^2-q_2^2)^2\right]\Bigg\}.
\end{aligned}
$$

For the object immediately in view we only need the terms involving x, y, z, and may therefore drop the first and last terms.

The expressions for q_s^2 and for $\mathfrak{T}_2^s$ in terms of κ^2 have been given above; by means of these I find that

$$
\frac{q_0'^2(\kappa^2-q_0^2)}{\mathfrak{T}_2}=\frac{9q_2^2}{4D\kappa^2},\qquad \frac{q_2'^2(\kappa^2-q_2^2)}{\mathfrak{T}_2^2}=-\frac{9q_0^2}{4D\kappa^2}
$$

(note the interchange in the suffixes of the q's).

A common factor $\frac{45}{4}\frac{q_0^2q_2^2}{D\kappa^2}$ may be taken from all the coefficients of x^2, y^2, z^2, and since $q_0^2q_2^2=\frac{1}{3}\kappa^2$ this common factor is equal to $15/4D$. Hence the terms in x^2, y^2, z^2 inside $\{\quad\}$ become

$$
\begin{aligned}
& +\frac{15}{4D}\frac{x^2}{k^2}\left[-\mathfrak{Q}_2\left(\frac{r}{k}\right)q_0'^2(\kappa^2-q_0^2)+\mathfrak{Q}_2^2\left(\frac{r}{k}\right)q_2'^2(\kappa^2-q_2^2)\right] \\
& +\frac{15}{4D}\frac{y^2}{k^2}\left[-\mathfrak{Q}_2\left(\frac{r}{k}\right)q_0'^2\qquad+\mathfrak{Q}_2^2\left(\frac{r}{k}\right)q_2'^2\right] \\
& +\frac{15}{4D}\frac{z^2}{k^2}\left[\mathfrak{Q}_2\left(\frac{r}{k}\right)\frac{q_0'^2}{q_0^2}(\kappa^2-q_0^2)-\mathfrak{Q}_2^2\left(\frac{r}{k}\right)\frac{q_2'^2}{q_2^2}(\kappa^2-q_2^2)\right].
\end{aligned}
$$

On substituting for the several coefficients their values in terms of κ, I find that the potential of M/λ may be written in the following form:—

$$\frac{M}{k\lambda}\left\{3\mathfrak{Q}_1\left(\frac{r}{k}\right)\cdot\frac{z}{k}+\tfrac{5}{4}\frac{x^2}{k^2}\left[-(2\kappa^2-1)\frac{\mathfrak{Q}_2-\mathfrak{Q}_2^{\,2}}{D}-(\mathfrak{Q}_2+\mathfrak{Q}_2^{\,2})\right]\right.$$
$$+\tfrac{5}{4}\frac{y^2}{k^2}\left[-(2-\kappa^2)\frac{\mathfrak{Q}_2-\mathfrak{Q}_2^{\,2}}{D}-(\mathfrak{Q}_2+\mathfrak{Q}_2^{\,2})\right]$$
$$\left.+\tfrac{5}{4}\frac{z^2}{k^2}\left[(1+\kappa^2)\frac{\mathfrak{Q}_2-\mathfrak{Q}_2^{\,2}}{D}+2(\mathfrak{Q}_2+\mathfrak{Q}_2^{\,2})\right]\right\} \quad . \quad . \quad . \quad . \quad (6).$$

It may be observed that this satisfies LAPLACE's equation, as it should do.

It remains to obtain approximate expressions for the $\mathfrak{Q}$'s.

The expression for these functions is given by

$$\mathfrak{Q}_i^s(\nu)=\mathfrak{P}_i^s(\nu)\int_\nu^\infty\frac{d\nu}{[\mathfrak{P}_i^s(\nu)]^2(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}}.$$

We require these when ν, which will be put equal to r/k, is large; thus we must develop in powers of $1/\nu$.

Now

$$(\nu^2-1)^{-1/2}(\nu^2-1/\kappa^2)^{-1/2}=\frac{1}{\nu^2}\left[1+\frac{1+\kappa^2}{2\kappa^2\nu^2}+\frac{3+2\kappa^2+3\kappa^4}{2^3\kappa^4\nu^4}+\frac{5+3\kappa^2+3\kappa^4+5\kappa^6}{2^4\kappa^6\nu^6}+\ldots\right].$$

Since $\mathfrak{P}_0(\nu)=1$, we have by integration

$$\mathfrak{Q}_0\left(\frac{r}{k}\right)=\frac{k}{r}\left[1+\frac{1+\kappa^2}{6\kappa^2}\cdot\frac{k^2}{r^2}+\frac{3+2\kappa^2+3\kappa^4}{40\kappa^4}\cdot\frac{k^4}{r^4}+\frac{5+3\kappa^2+3\kappa^4+5\kappa^6}{112\kappa^6}\cdot\frac{k^6}{r^6}+\ldots\right]. \quad (7).$$

There is no immediate need for this term, since it has been omitted above, but it will occur again hereafter.

Since $\mathfrak{P}_1(\nu)=\nu$, we have

$$3\mathfrak{Q}_1\left(\frac{r}{k}\right)=\frac{k^2}{r^2}\left[1+\frac{3(1+\kappa^2)}{10\kappa^2}\frac{k^2}{r^2}+\frac{3(3+2\kappa^2+3\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}+\ldots\right]. \quad . \quad . \quad . \quad (8).$$

Lastly, since $\mathfrak{P}_2^s(\nu)=\nu^2-q_s^2/\kappa^2$, we have

$$[\mathfrak{P}_2^s(\nu)]^{-2}=\frac{1}{\nu^4}\left[1+\frac{2q_s^2}{\kappa^2\nu^2}+\frac{3q_s^4}{\kappa^4\nu^4}+\ldots\right] \quad (s=0,\ 2),$$

so that

$$\frac{1}{[\mathfrak{P}_2^s(\nu)]^2(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}}$$
$$=\frac{1}{\nu^6}\left[1+\left(\frac{1+\kappa^2}{2\kappa^2}+\frac{2q_s^2}{\kappa^2}\right)\frac{1}{\nu^2}+\left(\frac{3+2\kappa^2+3\kappa^4}{8\kappa^4}+\frac{(1+\kappa^2)q_s^2}{\kappa^4}+\frac{3q_s^4}{\kappa^4}\right)\frac{1}{\nu^4}+\ldots\right](s=0,\ 2).$$

If we integrate this, multiply it by $\mathfrak{P}_2^s(\nu)$ and write r/k for ν, we find,

$$5\mathfrak{Q}_2^s\left(\frac{r}{k}\right)=\frac{k^3}{r^3}\left[1+\left\{\frac{5(1+\kappa^2)}{14\kappa^2}+\frac{3q_s^2}{7\kappa^2}\right\}\frac{k^2}{r^2}+5\left\{\frac{3+2\kappa^2+3\kappa^4}{72\kappa^4}+\frac{5q_s^2}{126\kappa^4}+\frac{q_s^4}{21\kappa^4}\right\}\frac{k^4}{r^4}\ldots\right](s=0,\ 2) \quad (9).$$

On substituting for q_s its value, I find

$$5\mathfrak{Q}_2^s\left(\frac{r}{k}\right) = \frac{k^3}{r^3}\left[1 + \frac{7(1+\kappa^2) \mp 2D}{14\kappa^2}\frac{k^2}{r^2} + \frac{5\{11+10\kappa^2+11\kappa^4 \mp 4(1+\kappa^2)D\}}{168\kappa^4}\frac{k^4}{r^4}\dots\right].$$

Whence

$$5[\mathfrak{Q}_2+\mathfrak{Q}_2^2] = \frac{2k^3}{r^3}\left[1 + \frac{1+\kappa^2}{2\kappa^2}\frac{k^2}{r^2} + \frac{5(11+10\kappa^2+11\kappa^4)}{168\kappa^4}\frac{k^4}{r^4}\dots\right],$$

$$\frac{5}{D}[\mathfrak{Q}_2-\mathfrak{Q}_2^2] = -\frac{2k^3}{r^3}\left[\quad\frac{1}{7\kappa^2}\frac{k^2}{r^2} + \frac{20(1+\kappa^2)}{168\kappa^4}\frac{k^4}{r^4}\dots\right].$$

Substituting these values in (6) we have for the potential of M/λ at the surface of the ellipsoid, as far as concerning terms involving x, y, z,

$$\begin{aligned}\frac{M}{\lambda k}\Bigg\{3\mathfrak{Q}_1\left(\frac{r}{k}\right)\cdot\frac{z}{k} &- \frac{x^2}{2k^2}\cdot\frac{k^3}{r^3}\left[1 + \frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2} + \frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\dots\right]\\ &- \frac{y^2}{2k^2}\cdot\frac{k^3}{r^3}\left[1 + \frac{3(1+3\kappa^2)}{14\kappa^2}\frac{k^2}{r^2} + \frac{5(5\kappa^4+2\kappa^2+1)}{56\kappa^4}\frac{k^4}{r^4}\dots\right]\\ &+ \frac{z^2}{k^2}\cdot\frac{k^3}{r^3}\left[1 + \frac{3(1+\kappa^2)}{7\kappa^2}\frac{k^2}{r^2} + \frac{5(3+2\kappa^2+3\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\dots\right]\Bigg\} \quad . \quad . \quad (10).\end{aligned}$$

If the system be rendered statical by the imposition of a rotation potential, we must add to the above such a potential, and that of the ellipsoid itself.

The expression for the internal potential of an ellipsoid ν_0 is given in (65) of "Harmonics"; it is

$$\frac{3M}{2k}\left\{\frac{\mathfrak{Q}_0(\nu_0)}{\mathfrak{P}_0(\nu_0)} - \frac{x^2}{k^2}\frac{\mathsf{Q}_1^1(\nu_0)}{\mathsf{P}_1^1(\nu_0)} - \frac{y^2}{k^2}\frac{\mathfrak{Q}_1^1(\nu_0)}{\mathfrak{P}_1^1(\nu_0)} - \frac{z^2}{k^2}\frac{\mathfrak{Q}_1(\nu_0)}{\mathfrak{P}_1(\nu_0)}\right\}.$$

I will now introduce an abridged notation which was used in some of my previous papers, as follows :-

$$\mathsf{P}_1^1(\nu_0)\,\mathsf{Q}_1^1(\nu_0) = \mathsf{A}_1^1, \quad \mathfrak{P}_1^1(\nu_0)\,\mathfrak{Q}_1^1(\nu_0) = \mathfrak{A}_1^1, \quad \mathfrak{P}_1(\nu_0)\,\mathfrak{Q}_1(\nu_0) = \mathfrak{A}_1.$$

Then, since

$$\mathsf{P}_1^1(\nu_0) = \sqrt{\left(\nu_0^2 - \frac{1}{\kappa^2}\right)}, \quad \mathfrak{P}_1^1(\nu_0) = \sqrt{(\nu_0^2-1)}, \quad \mathfrak{P}_1(\nu_0) = \nu_0,$$

we may, on omitting the term independent of x, y, z, write this potential in the form

$$-\frac{3M}{2k}\left[\frac{x^2}{k^2(\nu_0^2-1/\kappa^2)}\mathsf{A}_1^1 + \frac{y^2}{k^2(\nu_0^2-1)}\mathfrak{A}_1^1 + \frac{z^2}{k^2\nu_0^2}\mathfrak{A}_1\right] \quad . \quad . \quad . \quad . \quad (11)$$

The rotation with angular velocity ω takes place about an axis parallel to x through the centre of inertia of the system, which consists of two masses M and M/λ distant r from one another. Hence the rotation potential is

$$\tfrac{1}{2}\omega^2\left[y^2 + \left(z - \frac{r}{1+\lambda}\right)^2\right] = \frac{3M}{2k}\left\{\frac{\omega^2k^3}{3M}\left(\frac{y^2+z^2}{k^2}\right) - \tfrac{2}{3}\frac{\omega^2k^2r}{(1+\lambda)M}\cdot\frac{z}{k}\right\} + \frac{\omega^2r^2}{2(1+\lambda)^2} \cdot \quad (12).$$

The last term, being independent of x, y, z, has no present interest. Then, collecting results from (10), (11), and (12), the whole potential, as far as material, is

$$\begin{aligned}\tfrac{3}{2}\frac{M}{k}\Bigg[&\frac{2}{3\lambda}\left\{3\mathfrak{Q}_1\left(\frac{r}{k}\right)-\frac{\lambda\omega^2k^2r}{(1+\lambda)M}\right\}\frac{z}{k}\\ &-\frac{x^2}{k^2(\nu_0^2-1/\kappa^2)}\left\{\mathbf{A}_1^1+\frac{\nu_0^2-1/\kappa^2}{3\lambda}\frac{k^3}{r^3}\left[1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\cdots\right]\right\}\\ &-\frac{y^2}{k^2(\nu_0^2-1)}\left\{\mathfrak{A}_1^1+\frac{\nu_0^2-1}{3\lambda}\frac{k^3}{r^3}\left[1+\frac{3(3\kappa^2+1)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5\kappa^4+2\kappa^2+1)}{56\kappa^4}\frac{k^4}{r^4}\cdots\right]-\frac{\omega^2k^3}{3M}(\nu_0^2-1)\right\}\\ &-\frac{z^2}{k^2\nu_0^2}\left\{\mathfrak{A}_1-\frac{2\nu_0^2}{3\lambda}\frac{k^3}{r^3}\left[1+\frac{3(1+\kappa^2)}{7\kappa^2}\frac{k^2}{r^2}+\frac{5(3+2\kappa^2+3\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\cdots\right]-\frac{\omega^2k^3}{3M}\nu_0^2\right\}\Bigg].\end{aligned}$$

The condition that the figure of equilibrium should be the ellipsoid of reference is that this potential when equated to a constant should reproduce the equation to the ellipsoid. The coefficient of z must therefore vanish, and the three coefficients written inside { } must be equal to one another. These conditions give the angular velocity and equations for determining the figure, but as the subject will be reconsidered from a different point of view hereafter, I do not pursue the investigation here.

At present it need only be noted that the coefficient of z vanishes, and that the three coefficients are equal to one another. It is clear then that the potential U of the system, as rendered statical, may be written

$$\begin{aligned}U=-\frac{3M}{2k}&\left\{\mathbf{A}_1^1+\frac{\nu_0^2-1/\kappa^2}{3\lambda}\frac{k^3}{r^3}\left[1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\cdots\right]\right\}\\ &\times\left\{\frac{x^2}{k^2(\nu_0^2-1/\kappa^2)}+\frac{y^2}{k^2(\nu_0^2-1)}+\frac{z^2}{k^2\nu_0^2}\right\}.\end{aligned}$$

Now gravity g at the surface of the ellipsoid is $-dU/dn$, where n is the outward normal to the ellipsoid.

Hence

$$g=-\left[\frac{px}{k^2(\nu_0^2-1/\kappa^2)}\frac{\partial U}{\partial x}+\frac{py}{k^2(\nu_0^2-1)}\frac{\partial U}{\partial y}+\frac{pz}{k^2\nu_0^2}\frac{\partial U}{\partial z}\right].$$

Now

$$\frac{1}{p^2}=\frac{x^2}{k^4(\nu_0^2-1/\kappa^2)^2}+\frac{y^2}{k^4(\nu_0^2-1)^2}+\frac{z^2}{k^4\nu_0^4},$$

and in our alternative notation

$$\nu_0^2-\frac{1}{\kappa^2}=\frac{\cos^2\gamma}{\sin^2\beta}.$$

Therefore

$$g=\frac{3M}{pk}\left\{\mathbf{A}_1^1+\frac{k^3\cos^2\gamma}{3\lambda r^3\sin^2\beta}\left[1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}+\ldots\right]\right\}\quad . \quad (13).$$

As already remarked, we shall put $M = \frac{4}{3}\pi\rho a^3 \frac{\lambda}{1+\lambda}$; also, since the three axes of the ellipsoid are $k \cos\gamma \operatorname{cosec}\beta$, $k\cos\beta \operatorname{cosec}\beta$, $k \operatorname{cosec}\beta$, we have

$$\frac{k^3 \cos\beta\cos\gamma}{\sin^3\beta} = \frac{\lambda a^3}{1+\lambda}.$$

Hence

$$\frac{k^3\cos^2\gamma}{3\lambda r^3 \sin^2\beta} = \frac{a^3\cos\gamma\tan\beta}{3(1+\lambda)r^3},$$

and the coefficient of the series in the expression for g does not become infinite when λ vanishes; however, it is perhaps more convenient to leave it in the form as written above.

This expression for gravity is the result required, but it is to be noted that it is determined on the hypothesis that the distant body is a particle or sphere instead of being an ellipsoid.

The development ceases with terms of the seventh order, and the harmonic terms of third and higher orders have been neglected. Now the harmonic deformation of ROCHE's ellipsoid of the third order of harmonics is of order k^4/r^4 in inverse powers of r. This deformation is treated as surface density. If we were to proceed to closer approximation, we should have to take account of the square of the thickness of the layer; such terms would be of order k^8/r^8. Since, then, we are avowedly neglecting terms of this order, it is no use to carry the development higher than terms of the seventh order.

§ 6. *Form of the Expression for the Gravitational Lost Energy of the System.*

The system consists of two ellipsoids, say e and E, with their longest axes co-linear, and each of them is distorted by deformations expressible by ellipsoidal harmonics of orders higher than the second. To the order of approximation to be adopted these deformations may be replaced by layers of surface density, which may be denoted by l and L respectively.

The lost energy of the system may be represented symbolically by

$$V = \tfrac{1}{2}(e+l)^2 + \tfrac{1}{2}(E+L)^2 + (e+l)(E+L).$$

Let s, S denote two spheres of masses equal to e and E and concentric with them respectively.

Then the whole may be written

$$V = \tfrac{1}{2}ee + \tfrac{1}{2}EE + eE + \tfrac{1}{2}ll + \tfrac{1}{2}LL + (e+S)\,l + (E+s)\,L$$
$$+ (e-s)\,L + (E-S)\,l + lL.$$

In the term Sl I divide S into two parts, namely S_1, which is to contain all the terms in the potential of S at the surface of e excepting terms expressible by ellipsoidal harmonics of the second order with respect to the ellipsoid e; and S_2, which is to contain the omitted terms of the second order. Similarly, the term sL is to be divided into s_1L and s_2L.

Take the centre of e as origin of co-ordinates x, y, z with the z axis passing through the centre of E, the y axis coincident with the mean axis of e and the x axis coincident with the least axis of e.

Since l is expressible by harmonics higher than the second order, and since y^2+z^2 is expressible by harmonics of orders 0 and 2, it follows that the moment of inertia of the layer l about the axis is zero. If therefore ω is the angular velocity of the system, a contribution to the lost energy of the system which may be written symbolically $[\frac{1}{2}\omega^2(y^2+z^2)]\,l$ is zero.

It follows therefore that we may write

$$(e+S)\,l = [e+S_2+\tfrac{1}{2}\omega^2(y^2+z^2)]\,l+S_1l.$$

Similarly, if the ellipsoid E be referred to a parallel co-ordinate system X, Y, Z through its centre, and such that

$$x = X, \quad y = Y, \quad z = Z+r,$$

so that r is the distance between the two origins, we have

$$(E+s)\,L = [E+s_2+\tfrac{1}{2}\omega^2(Y^2+Z^2)]\,L+s_1L.$$

The problem is already so complicated that it will be convenient to omit certain small terms in the expression for the lost energy, which it would be very troublesome to evaluate.

The term $(e-s)\,L$ represents the mutual energy of the departure from sphericity of e with the layer of surface density L on E. This term is clearly very small and will be omitted. Similarly $(E-S)\,l$ will be neglected. It will appear from the results below that these terms are at least of the seventh order in powers of $1/r$. *À fortiori* lL, which is at least of the eighth order, will be omitted.

The whole expression for V will now be divided into several portions.

Let $(eE)_1$ be that portion of eE in which each ellipsoid may be replaced by a particle; it is, in fact, the product of the masses of e and E divided by r.

Let $(eE)_2$ be the rest of eE.

Let (vv) denote that portion of V in which the larger body E may be replaced by a sphere; then

$$(vv) = \tfrac{1}{2}ee+\tfrac{1}{2}ll+[e+S_2+\tfrac{1}{2}\omega^2(y^2+z^2)]\,l+S_1l.$$

Similarly, let

$$(VV) = \tfrac{1}{2}EE+\tfrac{1}{2}LL+[E+s_2+\tfrac{1}{2}\omega^2(Y^2+Z^2)]\,L+s_1L.$$

Then $V = (eE)_1+(eE)_2+(vv)+(VV)+$ neglected terms.

For ROCHE's problem, when the second body is a particle, V reduces to $(eE)_1+(vv)$, but in the modified form of the problem which I am going to solve the whole expression is required.

The evaluation of (eE) is so complicated that I devote a special section to it.

§ 7. *The Mutual Energy of Two Ellipsoids.*[*]

The semi-axes of the ellipsoid of mass e are to be denoted a, b, c, and the corresponding notation for the other ellipsoid is E, A, B, C. The distance between the centres of e and E is r; the axes c of e and C of E are in the same straight line, while a, A and b, B are respectively parallel. For brevity I imagine the densities of the ellipsoids to be unity.

If the external potential of e be U, and if $d\Omega$ be an element of volume or of mass of E, the lost energy to be evaluated is

$$(eE)=\int U d\Omega,$$

integrated throughout the ellipsoid E.

Let us suppose provisionally that the co-ordinates of the centres e and E are x, y, z and X, Y, Z, and let ξ, η, ζ be the co-ordinates of the element $d\Omega$; the axes being respectively parallel to a, b, c or A, B, C with arbitrary origin.

If $R^2=(\xi-x)^2+(\eta-y)^2+(\zeta-z)^2$, it is well known that the potential U of e at the point ξ, η, ζ is given by

$$U=e\sum_0^\infty\frac{3}{(2n+1)(2n+3)2n!}\left(a^2\frac{\partial^2}{\partial\xi^2}+b^2\frac{\partial^2}{\partial\eta^2}+c^2\frac{\partial^2}{\partial\zeta^2}\right)^n\frac{1}{R}.$$

Since $\frac{1}{R}$ satisfies LAPLACE's equation, we may eliminate $\frac{\partial^2}{\partial\zeta^2}$, and observing that $\frac{\partial^2}{\partial x^2}$, $\frac{\partial^2}{\partial y^2}$ are the same as $\frac{\partial^2}{\partial\xi^2}$, $\frac{\partial^2}{\partial\eta^2}$ respectively, we have

$$\begin{aligned}a^2\frac{\partial^2}{\partial\xi^2}+b^2\frac{\partial^2}{\partial\eta^2}+c^2\frac{\partial^2}{\partial\zeta^2}&=-(c^2-a^2)\frac{\partial^2}{\partial\xi^2}-(c^2-b^2)\frac{\partial^2}{\partial\eta^2}\\&=-k^2\left[\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right],\end{aligned}$$

It follows therefore that

$$U=e\sum_0^\infty\frac{(-)^n 3}{(2n+1)(2n+3)2n!}k^{2n}\left(\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)^n\frac{1}{R}.$$

Since the operator is independent of ξ, η, ζ, we have

$$(eE)=e\sum_0^\infty\frac{(-)^n 3}{(2n+1)(2n+3)2n!}k^{2n}\left(\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right)^n\cdot\int\frac{d\Omega}{R}.$$

---

[*] The results of this section were arrived at originally by a longer method. I have to thank one of the referees for showing me the following procedure.—*February* 26, 1906.

But $\int \frac{d\Omega}{R}$ is the potential of the ellipsoid E at the centre of the ellipsoid e, and by an exactly parallel transformation

$$\int \frac{d\Omega}{R} = E \sum_0^\infty \frac{(-)^n 3}{(2n+1)(2n+3)2n!} K^{2n} \left(\frac{1}{\mathrm{K}^2}\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)^n \frac{1}{\rho},$$

where $\rho^2 = (x-X)^2 + (y-Y)^2 + (z-Z)^2$.

Since our co-ordinate axes have a perfectly arbitrary origin, we may at once put $X = 0$, $Y = 0$, $Z = r$, $z = 0$, and after effecting the several differentiations put $x = 0$, $y = 0$.

It follows that, on putting $x = 0$, $y = 0$, after differentiation and writing $\rho^2 = x^2+y^2+r^2$,

$$(eE) = eE \sum_0^\infty \frac{(-)^n 3}{(2n+1)(2n+3)2n!} k^{2n} \left(\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)^n \sum_0^\infty \frac{(-)^i 3}{(2i+1)(2i+3)2i!} K^{2i} \left(\frac{1}{\mathrm{K}^2}\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)^i \frac{1}{\rho}.$$

If we denote the operator $\frac{1}{\kappa^2}\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ by d^2, and the operator $\frac{1}{\mathrm{K}^2}\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$ by D^2, we have

$$(eE) = eE\left[1 - \frac{1}{2.5}k^2\mathrm{d}^2 + \frac{1}{2^3.5.7}k^4\mathrm{d}^4 - \frac{1}{2^4.3^3.5.7}k^6\mathrm{d}^6 \ldots\right]$$

$$\left[1 - \frac{1}{2.5}K^2\mathrm{D}^2 + \frac{1}{2^3.5.7}K^4\mathrm{D}^4 - \frac{1}{2^4.3^3.5.7}K^6\mathrm{D}^6 \ldots\right]\frac{1}{\rho}$$

$$= eE\left[1 - \frac{1}{2.5}(k^2\mathrm{d}^2 + K^2\mathrm{D}^2) + \frac{1}{2^3.5.7}(k^4\mathrm{d}^4 + K^4\mathrm{D}^4) + \frac{1}{2^2.5^2}k^2K^2\mathrm{d}^2\mathrm{D}^2\right.$$

$$\left. - \frac{1}{2^4.3^3.5.7}(k^6\mathrm{d}^6 + K^6\mathrm{D}^6) - \frac{1}{2^4.5^2.7}(k^2K^4\mathrm{d}^2\mathrm{D}^4 + k^4K^2\mathrm{d}^4\mathrm{D}^2)\ldots\right]\frac{1}{\rho}.$$

On effecting the several differentiations, and putting $x = 0$, $y = 0$, we find

$$\mathrm{d}^2\frac{1}{\rho} = -\frac{1}{r^3}\left(\frac{1}{\kappa^2} + 1\right); \quad \mathrm{d}^4\frac{1}{\rho} = \frac{3}{r^5}\left(\frac{3}{\kappa^4} + \frac{2}{\kappa^2} + 3\right); \quad \mathrm{D}^2\mathrm{d}^2\frac{1}{\rho} = \frac{3}{r^5}\left(\frac{3}{\kappa^2\mathrm{K}^2} + \frac{1}{\kappa^2} + \frac{1}{\mathrm{K}^2} + 3\right);$$

$$\mathrm{d}^6\frac{1}{\rho} = -\frac{3^2.5}{r^7}\left(\frac{5}{\kappa^6} + \frac{3}{\kappa^4} + \frac{3}{\kappa^2} + 5\right); \quad \mathrm{d}^4\mathrm{D}^2\frac{1}{\rho} = -\frac{3^2.5}{r^7}\left(\frac{5}{\kappa^4\mathrm{K}^2} + \frac{1}{\kappa^4} + \frac{2}{\kappa^2\mathrm{K}^2} + \frac{2}{\kappa^2} + \frac{1}{\mathrm{K}^2} + 5\right);$$

and the remaining functions may be found by appropriate changes of small and large letters.

If now we again use ρ to denote the density of the spheroids, and revert to the notation employed elsewhere, namely,

$$e = \tfrac{4}{3}\pi\rho a^3 \frac{\lambda}{1+\lambda}, \quad E = \tfrac{4}{3}\pi\rho a^3 \frac{1}{1+\lambda},$$

we find

$$
\begin{aligned}
(eE) = (\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2 \frac{\lambda}{(1+\lambda)^2} \Bigg\{ 1 &+ \frac{1}{2.5r^3}\left[k^2\left(\frac{1}{\kappa^2}+1\right) + \mathcal{K}^2\left(\frac{1}{\mathrm{K}^2}+1\right)\right] \\
&+ \frac{3}{2^3.5.7r^5}\left[k^4\left(\frac{3}{\kappa^4}+\frac{2}{\kappa^2}+3\right) + \mathcal{K}^4\left(\frac{3}{\mathrm{K}^4}+\frac{2}{\mathrm{K}^2}+3\right)\right] \\
&+ \frac{3}{2^2.5^2r^5}\left[k^2\mathcal{K}^2\left(\frac{3}{\kappa^2\mathrm{K}^2}+\frac{1}{\kappa^2}+\frac{1}{\mathrm{K}^2}+3\right)\right] \\
&+ \frac{1}{2^4.3.7r^7}\left[k^6\left(\frac{5}{\kappa^6}+\frac{3}{\kappa^4}+\frac{3}{\kappa^2}+5\right) + \mathcal{K}^6\left(\frac{5}{\mathrm{K}^6}+\frac{3}{\mathrm{K}^4}+\frac{3}{\mathrm{K}^2}+5\right)\right] \\
&+ \frac{9}{2^4.5.7r^7}\Bigg[k^2\mathcal{K}^4\left(\frac{5}{\kappa^2\mathrm{K}^4}+\frac{1}{\mathrm{K}^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\mathrm{K}^2}+\frac{1}{\kappa^2}+5\right) \\
&\qquad + k^4\mathcal{K}^2\left(\frac{5}{\kappa^4\mathrm{K}^2}+\frac{1}{\kappa^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\kappa^2}+\frac{1}{\mathrm{K}^2}+5\right)\Bigg]\Bigg\} \quad (14).
\end{aligned}
$$

The first term in this expression is that which was called above $(eE)_1$, and the rest constitutes $(eE)_2$.

If the body E were a sphere, the only portions of (14) which would remain would be the parts of the expression independent of $\mathcal{K}$.

With the object of effecting certain differentiations hereafter, it is desirable that the formula for (eE) should be expressed in terms of the semi-axes a, b, c and A, B, C.

In accordance with the notation used elsewhere, we have

$$
a = \frac{k\cos\gamma}{\sin\beta}, \quad b = \frac{k\cos\beta}{\sin\beta}, \quad c = \frac{k}{\sin\beta}, \quad \text{where } \sin\beta = \kappa\sin\gamma,
$$

$$
A = \frac{\mathcal{K}\cos\Gamma}{\sin\mathrm{B}}, \quad B = \frac{\mathcal{K}\cos\mathrm{B}}{\sin\mathrm{B}}, \quad C = \frac{\mathcal{K}}{\sin\mathrm{B}}, \quad \text{where } \sin\mathrm{B} = \mathrm{K}\sin\Gamma.^*
$$

The result of the translation into this other notation is as follows :—

$$
\begin{aligned}
(eE) = (\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2 \frac{\lambda}{(1+\lambda)^2} \Bigg\{ 1 &+ \frac{1}{2.5r^3}[2c^2-a^2-b^2+\text{same in } A,\ B,\ C] \\
&+ \frac{3}{2^3.5.7r^5}[3(a^4+b^4)+8c^4-8c^2(a^2+b^2)+2a^2b^2+\text{same in } A, B, C] \\
&+ \frac{3}{2^2.5^2r^5}[2(A^2a^2+B^2b^2+C^2c^2)+(A^2+B^2+C^2)(a^2+b^2+c^2) \\
&\qquad -5C^2(a^2+b^2)-5c^2(A^2+B^2)+5C^2c^2] \\
&+ \frac{1}{2^4.3.7r^7}[16c^6-5(a^6+b^6)-24c^4(a^2+b^2)+18c^2(a^4+b^4) \\
&\qquad -3a^2b^2(a^2+b^2)+12a^2b^2c^2+\text{same in } A,\ B,\ C] \\
&+ \frac{9}{2^4.5.7r^7}[-A^4(5a^2+b^2-6c^2)-B^4(a^2+5b^2-6c^2) \\
&\qquad -8C^4(a^2+b^2-2c^2)+4B^2C^2(a^2+3b^2-4c^2) \\
&\qquad +4C^2A^2(3a^2+b^2-4c^2)-2A^2B^2(a^2+b^2+2c^2) \\
&\qquad +\text{same with small and large letters interchanged}]\Bigg\} \quad \ldots\ldots\ldots \quad (15).
\end{aligned}
$$

---

* The fact that capital β is nearly the same as B must be pardoned; it cannot, I think, cause any confusion.

§ 8. *Remaining Terms in the Expression for the Lost Energy.*

If e be the mass of an ellipsoid of semi-axes a, b, e, the lost energy of its concentration is

$$\tfrac{1}{2}(ee) = \tfrac{3}{10}e^2\psi,$$

where

$$\psi = \int_0^\infty \frac{du}{(u+a^2)^{1/2}(u+b^2)^{1/2}(u+e^2)^{1/2}}.$$

In the present case

$$e = \tfrac{4}{3}\pi\rho\mathrm{a}^3\frac{\lambda}{1+\lambda},$$

and

$$\psi = \frac{2}{k}\int_{\nu_0}^\infty \frac{d\nu}{(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}},$$

where

$$\nu_0 = \frac{1}{\kappa\sin\gamma} = \frac{1}{\sin\beta}.$$

Thus

$$\tfrac{1}{2}(ee) = \tfrac{3}{10}(\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda^2}{(1+\lambda)^2}\psi \quad \ldots\ldots\ldots \quad (16).$$

By symmetry

$$\tfrac{1}{2}(EE) = \tfrac{3}{10}(\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{1}{(1+\lambda)^2}\Psi \quad \ldots\ldots\ldots \quad (17),$$

where

$$\Psi = \frac{2}{K}\int_{\mathrm{N}_0}^\infty \frac{d\mathrm{N}}{(\mathrm{N}^2-1)^{1/2}(\mathrm{N}^2-1/\mathrm{K}^2)^{1/2}},$$

and

$$\mathrm{N}_0 = \frac{1}{\mathrm{K}\sin\Gamma} = \frac{1}{\sin\mathrm{B}}.$$

The lost energy (lS_1) is the potential of a particle S, equal in mass to E placed at the centre of E, with the omission of terms of the second order of harmonics, multiplied by the density of the layer l and integrated over the surface of e. This is the same as the potential of the layer l, with the omission of harmonic terms of the second order (and there are none such) at the centre of E multiplied by the mass of E.

A typical term in the surface density representing the layer l is, say,

$$f_i^s\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi).$$

The external potential corresponding to such a term, at the point ν, μ, ϕ, is by (51) of "Harmonics,"

$$\frac{3}{k}\left(\tfrac{4}{3}\pi\rho\mathrm{a}^3\frac{\lambda}{1+\lambda}\right)f_i^s\mathfrak{Q}_i^s(\nu)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi).$$

The co-ordinates of the centre of E are $\nu = \frac{r}{k}$, $\mu = 1$, $\phi = \frac{1}{2}\pi$; and the mass of E is $\frac{4}{3}\pi\rho\mathrm{a}^3/(1+\lambda)$.

Hence the contribution to (lS_1) corresponding to this term is

$$\frac{3}{k}\left(\tfrac{4}{3}\pi\rho a^3\right)^2 \frac{\lambda}{(1+\lambda)^2} f_i^s \mathfrak{Q}_i^s(r/k) \mathfrak{P}_i^s(\nu_0) \mathfrak{P}_i^s(1) \mathfrak{C}_i^s(\tfrac{1}{2}\pi).$$

Now $\mathfrak{P}_i^s(1)\mathfrak{C}_i^s(\frac{1}{2}\pi)$ vanishes for all harmonics except cosine-harmonics of even rank. Therefore

$$(lS_1) = \frac{3}{k}\left(\tfrac{4}{3}\pi\rho a^3\right)^2 \frac{\lambda}{(1+\lambda)^2} \Sigma f_i^s \mathfrak{Q}_i^s(r/k) \mathfrak{P}_i^s(\nu_0) \mathfrak{P}_i^s(1) \begin{Bmatrix} \mathfrak{C}_i^s \\ \mathsf{C}_i^s \end{Bmatrix} (\tfrac{1}{2}\pi) \begin{Bmatrix} i \text{ even} \\ i \text{ odd} \end{Bmatrix} \quad . \quad . \quad (18),$$

the summation being for all values of i greater than 2, and for all even values of s.

The lost energy (Ls_1) is expressible by the similar function for the other ellipsoid, but I have not adopted a specific notation for the ellipsoidal harmonics for the ellipsoid E, and therefore cannot write down the result.

The lost energy $(e+S_2+\frac{1}{2}\omega^2(y^2+z^2))l$ is the potential of the ellipsoid e, together with the potential of S in as far as it involves harmonics of the second order, and a rotation potential, multiplied by the density of the layer l, and integrated over the surface of e. That is to say it is the potential of gravity on the ellipsoid e integrated throughout the layer l, which it is not permissible to regard as surface density.

If the thickness of the layer be ζ, and if $d\zeta$ be a slice of that part of the layer which is erected normally on an element $d\sigma$ of the surface e, then $\rho\, d\zeta\, d\sigma$ is an element of mass of the layer. The potential of gravity is $-g\zeta$. Hence the lost energy is

$$-\rho \iint_0^\zeta g\zeta\, d\zeta\, d\sigma = -\tfrac{1}{2}\rho \int g\zeta^2\, d\sigma.$$

Accordingly the lost energy is equal and opposite to the work done in raising the layer, considered as surface density, through half its thickness, against gravity.

We may take as a typical term

$$\zeta = pf_i^s \mathfrak{P}_i^s(\mu) \mathfrak{C}_i^s(\phi),$$

and we have shown in (13) that

$$g = \frac{3}{pk}\tfrac{4}{3}\pi\rho a^3 \frac{\lambda}{1+\lambda}\left\{\mathsf{A}_1{}^1 + \frac{k^3}{3\lambda r^3}\frac{\cos^2\gamma}{\cos^2\beta}\left[1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\ldots\right]\right\}.$$

It should be noted that this expression for gravity takes no account of the change in the ellipticity of e which is due to the fact that E is an ellipsoid and not a sphere. The error introduced thus is however outside the limits of accuracy which have been adopted.

Accordingly this portion of the lost energy is

$$-\frac{3}{2k}\tfrac{4}{3}\pi\rho^2 a^3 \frac{\lambda}{1+\lambda}(f_i^s)^2\{\mathsf{A}_1{}^1+\text{series}\}\int[\mathfrak{P}_i^s(\mu)\mathfrak{C}_i^s(\phi)]^2 p\, d\sigma.$$

Now in § 5 we defined

$$\mathfrak{T}_i^s = \frac{(2i+1)}{4\pi \mathrm{a}^3\lambda/(1+\lambda)}\int [\mathfrak{P}_i^s(\mu)\mathfrak{C}_i^s(\phi)]^2 p\, d\sigma.$$

Hence

$$(e+S_2+\tfrac{1}{2}\omega^2(y^2+z^2))\, l = -\frac{9}{2k}(\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2 \frac{\lambda^2}{(1+\lambda)^2}\Sigma\frac{(f_i^s)^2}{2i+1}\{\mathsf{A}_1{}^1+\text{series}\}\,\mathfrak{T}_i^s \quad . \quad (19),$$

the summation being for all harmonics.

In determining the lost energy $\frac{1}{2}(ll)$ we may treat the layer as surface density. A typical term in the surface density is $\rho p f_i^s \mathfrak{P}_i^s(\mu)\mathfrak{C}_i^s(\phi)$, and the surface value of its potential is

$$\frac{3}{k}(\tfrac{4}{3}\pi\rho \mathrm{a}^3)\frac{\lambda}{1+\lambda} f_i^s \mathfrak{P}_i^s(\nu_0)\mathfrak{Q}_i^s(\nu_0)\mathfrak{P}_i^s(\mu)\mathfrak{C}_i^s(\phi).$$

Then, since

$$\mathfrak{A}_i^s = \mathfrak{P}_i^s(\nu_0)\mathfrak{Q}_i^s(\nu_0),$$

a typical term of $\frac{1}{2}(ll)$ is

$$\frac{3\rho}{2k}(\tfrac{4}{3}\pi\rho \mathrm{a}^3)\frac{\lambda}{1+\lambda}(f_i^s)^2\mathfrak{A}_i^s\int [\mathfrak{P}_i^s(\mu)\mathfrak{C}_i^s(\phi)]^2 p\, d\sigma.$$

Thus

$$\tfrac{1}{2}(ll) = \frac{9}{2k}(\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2\frac{\lambda^2}{(1+\lambda)^2}\Sigma\frac{(f_i^s)^2}{2i+1}\mathfrak{A}_i^s\mathfrak{T}_i^s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20),$$

the summation being made for all harmonics.

The value of $\frac{1}{2}(LL)$ may be written down by symmetry.

§ 9. *Final Expression for the Lost Energy of the System.*

We have

$$V = (eE)_1 + (vv) + (VV) + (eE)_2.$$

The several parts are to be collected from (14) or (15), (16), (17), (18), (19), (20), and we have

$$(eE)_1 = (\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2 r},$$

$$(vv) = (\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\Big\{\tfrac{3}{10}\lambda\psi + \frac{3}{k}\Sigma f_i^s\mathfrak{Q}_i^s(r/k)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi) \quad (i>2,\ s \text{ even})$$

$$+\tfrac{9}{2}\frac{\lambda}{k}\Sigma\frac{(f_i^s)^2\mathfrak{T}_i^s}{2i+1}\left[\mathfrak{A}_i^s - \mathsf{A}_1{}^1 - \frac{k^3\cos^2\gamma}{3\lambda r^3\sin^2\beta}\left(1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\right)\right]\begin{matrix}\text{(all}\\ \text{harm.)}\end{matrix}\Big\},$$

(VV)= symmetrical expression with $1/\lambda$ in place of λ.

$$
\begin{aligned}
(eE)_2 = (\tfrac{4}{3}\pi\rho \mathrm{a}^3)^2 \frac{\lambda}{(1+\lambda)^2} \Bigg\{ & \frac{1}{2.5r^3}\left[k^2\left(\frac{1}{\kappa^2}+1\right)+K^2\left(\frac{1}{\mathrm{K}^2}+1\right)\right] \\
& + \frac{3}{2^3.5.7r^5}\left[k^4\left(\frac{3}{\kappa^4}+\frac{2}{\kappa^2}+3\right)+K^4\left(\frac{3}{\mathrm{K}^4}+\frac{2}{\mathrm{K}^2}+3\right)\right] \\
& + \frac{3}{2^2.5^2r^5}k^2K^2\left(\frac{3}{\kappa^2\mathrm{K}^2}+\frac{1}{\mathrm{K}^2}+\frac{1}{\kappa^2}+3\right) \\
& + \frac{1}{2^4.3.7r^7}\left[k^6\left(\frac{5}{\kappa^6}+\frac{3}{\kappa^4}+\frac{3}{\kappa^2}+5\right)+K^6\left(\frac{5}{\mathrm{K}^6}+\frac{3}{\mathrm{K}^4}+\frac{3}{\mathrm{K}^2}+5\right)\right] \\
& + \frac{9}{2^4.5.7r^7}\left[k^2K^4\left(\frac{5}{\kappa^2\mathrm{K}^4}+\frac{1}{\mathrm{K}^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\mathrm{K}^2}+\frac{1}{\kappa^2}+5\right)\right. \\
& \left.\qquad + k^4K^2\left(\frac{5}{\mathrm{K}^2\kappa^4}+\frac{1}{\kappa^4}+\frac{2}{\mathrm{K}^2\kappa^2}+\frac{2}{\kappa^2}+\frac{1}{\mathrm{K}^2}+5\right)\right]\Bigg\} \quad (21).
\end{aligned}
$$

§ 10. *Determination of the Forms of the Ellipsoids.*

We have obtained in the last section the expression for V, the lost energy of the system.

The harmonic deformations of the ellipsoids being of orders higher than the second do not enter into the moment of inertia to the order of approximation adopted. Hence the moment of inertia about the axis of rotation, which passes through the centre of inertia of the system, and is parallel to the a and A axes of the ellipsoids, is given by

$$I = \tfrac{4}{3}\pi\rho \mathrm{a}^3\left[\tfrac{1}{5}\frac{\lambda}{1+\lambda}(b^2+c^2)+\tfrac{1}{5}\frac{1}{1+\lambda}(B^2+C^2)+\frac{\lambda r^2}{(1+\lambda)^2}\right]. \quad . \quad . \quad . \quad (22).$$

If f denotes any one of the parameters by which the system is defined, the condition that the figures shall be in equilibrium is

$$\frac{\partial V}{\partial f}+\tfrac{1}{2}\omega^2\frac{\partial I}{\partial f} = 0.$$

The parameters defining the system may be taken as r, the distance between the two centres, $\cos\gamma$, $\cos\beta$ for the smaller ellipsoid and $\cos\Gamma$, $\cos \mathrm{B}$ for the larger one. Besides these we have the coefficients f_i^s, F_i^s of the harmonic inequalities of order i and rank s on the two ellipsoids.

For convenience write

$$\mathfrak{a} = \cos\gamma, \quad \mathfrak{b} = \cos\beta.$$

These letters are chosen on account of the association of $\cos\gamma$, $\cos\beta$ with the semi-axes a, b of the smaller ellipsoid e. It is unnecessary to adopt a corresponding notation for the ellipsoid E, because, when the problem is solved as regards e, it affords the solution for E by symmetry.

Since

$$k^3\cos\beta\cos\gamma\operatorname{cosec}^3\beta = \lambda \mathrm{a}^3/(1+\lambda),$$

we have

$$\frac{k}{\mathrm{a}} = \left(\frac{\lambda}{1+\lambda}\right)^{1/3} \frac{(1-\mathfrak{b}^2)^{1/2}}{(\mathfrak{a}\mathfrak{b})^{1/3}}.$$

Hence

$$\frac{a}{\mathrm{a}} = \frac{k}{\mathrm{a}}\frac{\cos\gamma}{\sin\beta} = \left(\frac{\lambda}{1+\lambda}\right)^{1/3} \frac{\mathfrak{a}^{2/3}}{\mathfrak{b}^{1/3}}, \quad \frac{b}{\mathrm{a}} = \frac{k}{\mathrm{a}}\frac{\cos\beta}{\sin\beta} = \left(\frac{\lambda}{1+\lambda}\right)^{1/3} \frac{\mathfrak{b}^{2/3}}{\mathfrak{a}^{1/3}}, \quad \frac{c}{\mathrm{a}} = \frac{k}{\mathrm{a}\sin\beta} = \left(\frac{\lambda}{1+\lambda}\right)^{1/3} \frac{1}{(\mathfrak{a}\mathfrak{b})^{1/3}}.$$

Therefore

$$3\frac{da}{a} = 2\frac{d\mathfrak{a}}{\mathfrak{a}} - \frac{d\mathfrak{b}}{\mathfrak{b}}, \quad 3\frac{db}{b} = -\frac{d\mathfrak{a}}{\mathfrak{a}} + 2\frac{d\mathfrak{b}}{\mathfrak{b}}, \quad 3\frac{dc}{c} = -\frac{d\mathfrak{a}}{\mathfrak{a}} - \frac{d\mathfrak{b}}{\mathfrak{b}}.$$

Therefore

$$3\mathfrak{a}\frac{\partial}{\partial\mathfrak{a}} = 2a\frac{\partial}{\partial a} - b\frac{\partial}{\partial b} - c\frac{\partial}{\partial c}; \quad 3\mathfrak{b}\frac{\partial}{\partial\mathfrak{b}} = -a\frac{\partial}{\partial a} + 2b\frac{\partial}{\partial b} - c\frac{\partial}{\partial c} \quad . \quad . \quad . \quad (23).$$

These enable us to differentiate, with respect to $\mathfrak{a}$, $\mathfrak{b}$, functions expressed in terms of a, b, c; the parameters r, f_i^s always occur explicitly.

The equation of condition for the parameter r is

$$\frac{\partial V}{\partial r} + \tfrac{1}{2}\omega^2\frac{\partial I}{\partial r} = 0.$$

On differentiating (22) we have

$$\tfrac{1}{2}\omega^2\frac{\partial I}{\partial r} = \tfrac{4}{3}\pi\rho\mathrm{a}^3\frac{\lambda\omega^2 r}{(1+\lambda)^2}.$$

In order to differentiate V we must take separately its several portions as defined in (21).

Now

$$-\frac{\partial}{\partial r}(eE)_1 = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2 r^2}$$

$$-\frac{\partial}{\partial r}(vv) = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left\{-\frac{3}{k}\Sigma f_i^s\mathfrak{P}_i^s(\nu_0)\mathfrak{P}_i^s(1)\mathfrak{C}_i^s(\tfrac{1}{2}\pi)\frac{d}{dr}\mathfrak{Q}_i^s\left(\frac{r}{k}\right) \quad (i>2,\ s\text{ even})\right.$$

$$\left. + \tfrac{9}{2}\frac{k^2}{r^4}\Sigma\frac{(f_i^s)^2\,\mathfrak{T}_i^s}{2i+1}\frac{\cos^2\gamma}{\sin^2\beta}\left[1 + \frac{5(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2} + \frac{5(5+2\kappa^2+\kappa^4)}{56\kappa^4}\frac{k^4}{r^4}\ldots\right](\text{all harm.})\right\}$$

$$-\frac{\partial}{\partial r}(VV) = \text{symmetrical expression for larger ellipsoid.}$$

$$-\frac{\partial}{\partial r}(eE)_2 = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left\{\frac{3}{2.5r^4}\left[k^2\left(\frac{1}{\kappa^2}+1\right) + K^2\left(\frac{1}{\mathrm{K}^2}+1\right)\right]\right.$$

$$+ \frac{3}{2^3.7r^6}\left[k^4\left(\frac{3}{\kappa^4}+\frac{2}{\kappa^2}+3\right) + K^4\left(\frac{3}{\mathrm{K}^4}+\frac{2}{\mathrm{K}^2}+3\right)\right]$$

$$+ \frac{3}{2^2.5r^6}k^2K^2\left(\frac{3}{\kappa^2\mathrm{K}^2}+\frac{1}{\kappa^2}+\frac{1}{\mathrm{K}^2}+3\right)$$

$$+ \frac{1}{2^4.3r^8}\left[k^6\left(\frac{5}{\kappa^6}+\frac{3}{\kappa^4}+\frac{3}{\kappa^2}+5\right) + K^6\left(\frac{5}{\mathrm{K}^6}+\frac{3}{\mathrm{K}^4}+\frac{3}{\mathrm{K}^2}+5\right)\right]$$

$$+ \frac{9}{2^4.5r^8}\left[k^2K^4\left(\frac{5}{\kappa^2\mathrm{K}^4}+\frac{1}{\mathrm{K}^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\mathrm{K}^2}+\frac{1}{\kappa^2}+5\right)\right.$$

$$\left.\left. + k^4K^2\left(\frac{5}{\mathrm{K}^2\kappa^4}+\frac{1}{\kappa^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\kappa^2}+\frac{1}{\mathrm{K}^2}+5\right)\right]\right\}.$$

The sum of these last four expressions is equal to $-\partial V/\partial r$, and therefore equal to $\frac{1}{2}\omega^2\,\partial I/\partial r$.

Now let

$$\omega^2 r^3 = \tfrac{4}{3}\pi\rho a^3(1+\zeta),$$

so that ζ represents the correction to KEPLER'S law of periodic times on account of the ellipticity of the two bodies. Then we have

$$\begin{aligned}\zeta = {} & \frac{3}{10r^2}\left[k^2\left(\frac{1}{\kappa^2}+1\right)+K^2\left(\frac{1}{\mathrm{K}^2}+1\right)\right]+\frac{3}{56r^4}\left[k^4\left(\frac{3}{\kappa^4}+\frac{2}{\kappa^2}+3\right)+K^4\left(\frac{3}{\mathrm{K}^4}+\frac{2}{\mathrm{K}^2}+3\right)\right] \\ & +\frac{3}{20r^4}k^2K^2\left(\frac{3}{\kappa^2\mathrm{K}^2}+\frac{1}{\mathrm{K}^2}+\frac{1}{\kappa^2}+3\right)+\frac{1}{48r^6}\left[k^6\left(\frac{5}{\kappa^6}+\frac{3}{\kappa^4}+\frac{3}{\kappa^2}+5\right)+K^6\left(\frac{5}{\mathrm{K}^6}+\frac{3}{\mathrm{K}^4}+\frac{3}{\mathrm{K}^2}+5\right)\right] \\ & +\frac{9}{80r^6}\left[k^2K^4\left(\frac{5}{\kappa^2\mathrm{K}^4}+\frac{1}{\mathrm{K}^4}+\frac{2}{\mathrm{K}^2\kappa^2}+\frac{2}{\mathrm{K}^2}+\frac{1}{\kappa^2}+5\right)+k^4K^2\left(\frac{5}{\mathrm{K}^2\kappa^4}+\frac{1}{\kappa^4}+\frac{2}{\mathrm{K}^2\kappa^2}+\frac{2}{\kappa^2}+\frac{1}{\mathrm{K}^2}+5\right)\right] \\ & -\frac{3}{k}\Sigma f_i^s\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)\,r^2\frac{d}{dr}\mathfrak{Q}_i^s\left(\frac{r}{k}\right) \quad (i>2,\ s\text{ even}) \\ & +\tfrac{9}{2}\frac{k^2}{r^2}\Sigma\frac{(f_i^s)^2\,\mathfrak{T}_i^s}{2i+1}\frac{\cos^2\gamma}{\sin^2\beta}\left\{1+\frac{5(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}+\dots\right\} \quad (\text{all harmonics}) \quad . \quad . \quad . \quad . \quad (24)\end{aligned}$$

When $\mathfrak{Q}_i^s(r/k)$ is developed in powers of $1/r$, its first term is one in $r^{-(i+1)}$; hence $r^2\dfrac{\partial}{\partial r}\mathfrak{Q}_i^s$ begins with r^{-i}. Now f_i^s will be determined from terms in the potential of the ellipsoid E of the i^{th} order of harmonics, and will therefore involve $r^{-(i+1)}$. Therefore in the series contained in the last term but one of ζ each term is of order $r^{-(2i+1)}$. Since the lowest value of i is 3, the term of lowest order in this series is one in r^{-7}, and as I shall not attempt to evaluate ζ beyond r^{-6} the whole of this series is negligible.

Again, since $(f_i^s)^2$ is of order r^{-2i-2}, and since r^{-2} occurs as a factor, each term is of order r^{-2i-4}. Thus the lowest term is of order r^{-10} and is negligible.*

It follows that the only sensible part of ζ arises from the portion of V denoted $(eE)_2$, and the last two terms of (24) may be erased.

We next consider the parameter f_i^s, and, since I does not involve it, the equation reduces to $\partial V/\partial f_i^s = 0$; or, since V only contains f_i^s in the part denoted (vv), it becomes $\partial(vv)/\partial f_i^s = 0$.

This gives, for $i>2$, s even

$$f_i^s = -\tfrac{1}{3}(2i+1)\frac{\mathfrak{Q}_i^s(r/k)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)}{\lambda\mathfrak{T}_i^s\left\{\mathfrak{A}_i^s-\mathsf{A}_1^1-\dfrac{k^3}{3\lambda r^3}\dfrac{\cos^2\gamma}{\sin^2\beta}\left[1+\dfrac{3(3+\kappa^2)}{14\kappa^2}\dfrac{k^2}{r^2}+\dots\right]\right\}} \quad . \quad (25).$$

Since this formula contains λ in the denominator, it would appear at first sight as if

---

* It is proper to remark that the terms retained in ζ are really of higher orders than they appear to be. I recur to the neglected portions of ζ hereafter in § 23.

f_i^s became infinite when $\lambda = 0$. But this is not so, because when $\mathfrak{Q}_i^s(r/k)$ is developed the first term of the series is one in $(k/r)^{i+1}$; now $k^3 = \frac{\lambda}{1+\lambda}\mathrm{a}^3 \sin^3\beta \sec\beta \sec\gamma$, and therefore the formula for f_i^s involves the factor $\left(\frac{\lambda}{1+\lambda}\right)^{(i+1)/3} \cdot \frac{1}{\lambda}$ or $\left(\frac{\lambda}{1+\lambda}\right)^{(i-2)/3} \cdot \frac{1}{1+\lambda}$. We see then that f_i^s vanishes both when $\lambda = 0$ and $\lambda = \infty$.

This factor is a maximum when $\lambda = \frac{1}{3}(i-2)$. Therefore we should expect, *cæteris paribus*, the third harmonics to be most important when $\lambda = \frac{1}{3}$, the fourth when $\lambda = \frac{2}{3}$, the fifth when $\lambda = 1$, and the higher harmonics when λ is greater than unity. This prevision is partially fulfilled by the numerical results given below, but it was not to be expected that it should be exactly so, because the other conditions are not exactly the same in the solutions for various values of λ.

The formula shows, as stated above, that f_i^s is of order r^{-i-1}. The series in the denominator affects the result but slightly and might be omitted, except, perhaps, in the case of the third zonal harmonic. For all harmonics other than cosine-harmonics of even rank f_i^s is zero.

It is now possible to eliminate f_i^s from (vv) by substituting for it its value. These terms in (vv) become, in this way, equal to

$$\left(\tfrac{4}{3}\pi\rho\mathrm{a}^3\right)^2 \frac{\lambda}{(1+\lambda)^2}\left\{-\frac{2i+1}{2k\lambda}\,\frac{\left[\mathfrak{Q}_i^s\left(\frac{r}{k}\right)\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s\left(\tfrac{1}{2}\pi\right)\right]^2}{\mathfrak{T}_i^s\left[\mathfrak{A}_i^s - \mathsf{A}_1^1 - \text{series}\right]}\right\} \quad . \quad . \quad (26).$$

When $i = 3$, this term is of order r^{-8}, and is negligible; hence we need no longer pay any attention to the inequalities on the ellipsoid. However, the formula (25) is important as rendering it possible to evaluate the inequalities.

Since for all inequalities, excepting cosine-harmonics of even rank, f_i^s only occurs in the energy function as a square, it is in these cases a principal co-ordinate, and $(\mathfrak{A}_i^s - \mathsf{A}_1^1 - \textit{series})$ is a coefficient of stability.

But the like is not true for the cosine-harmonics of even rank, because, when we consider, for example, the harmonics of the third order, we see that $\partial^2 V/df_3^s dr$ is of the fifth order and $\partial^2 V/\partial f_3^s \partial\mathfrak{a}$, $\partial^2 V/\partial f_3^s \partial\mathfrak{b}$ $(s = 0, 2)$ are of the fourth order.

It is clear that the inequalities on the ellipsoid E are determinable by symmetrical formulæ.

We must now turn to the equations of equilibrium for the parameters $\mathfrak{a}$ and $\mathfrak{b}$. Since differentiation with respect to these parameters is effected most conveniently by means of the formulæ (23), the portion of V called $(eE)_2$ should be written in the form (15). After effecting the differentiations it is, however, best to revert to the notation involving k, κ, γ, $\mathcal{K}$, K, Γ; but as an exception to the general rule as to notation, it is most convenient to retain the differentials of $k^2(1+1/\kappa^2)$ and of b^2+c^2 in the forms involving a, b, c. As the algebraic processes involved are rather long, I simply give the results, as follows:—

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}(b^2+c^2) = -2\,(b^2+c^2)\;\ldots\;(\text{i}),$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}(b^2+c^2) = 2\,(2b^2-c^2)\;\ldots\;(\text{i})'.$$

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}k^2\left(\frac{1}{\kappa^2}+1\right) = 2\,(b^2-2a^2-2c^2)\;\ldots\;(\text{ii}),$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}k^2\left(\frac{1}{\kappa^2}+1\right) = 2\,(a^2-2b^2-2c^2)\;\ldots\;(\text{ii})'.$$

The remaining results are expressed in terms of k, κ, γ, &c.

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}k^4\left(\frac{3}{\kappa^4}+\frac{2}{\kappa^2}+3\right) = \frac{4k^4}{\kappa^4\sin^2\gamma}\left[-3\,(3+\kappa^2)+(6+\kappa^2-3\kappa^4)\sin^2\gamma\right]\;\ldots\;(\text{iii}),$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}\quad\text{same}\quad = \frac{4k^4}{\kappa^4\sin^2\gamma}\left[-3\,(3\kappa^2+1)+(6\kappa^4+\kappa^2-3)\sin^2\gamma\right]\;\ldots\;(\text{iii})'.$$

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}k^6\left(\frac{5}{\kappa^6}+\frac{3}{\kappa^4}+\frac{3}{\kappa^2}+5\right) = \frac{6k^6}{\kappa^6\sin^2\gamma}\left[-3\,(5+2\kappa^2+\kappa^4)+(10+3\kappa^2+0\kappa^4-5\kappa^6)\sin^2\gamma\right]\;\ldots\;(\text{iv}),$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}\quad\text{same}\quad = \frac{6k^6}{\kappa^6\sin^2\gamma}\left[-3(5\kappa^4+2\kappa^2+1)+(10\kappa^6+3\kappa^4+0\kappa^2-5)\sin^2\gamma\right]\ldots(\text{iv})'.$$

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}k^2\mathcal{K}^2\left(\frac{3}{\kappa^2\mathrm{K}^2}+\frac{1}{\mathrm{K}^2}+\frac{1}{\kappa^2}+3\right) = \frac{2k^2\mathcal{K}^2}{\kappa^2\mathrm{K}^2\sin^2\gamma}\left[-(3+\mathrm{K}^2)(3-2\sin^2\gamma)-\kappa^2(1+3\mathrm{K}^2)\sin^2\gamma\right]\ldots(\text{v}),$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}\quad\text{same}\quad = \frac{2k^2\mathcal{K}^2}{\kappa^2\mathrm{K}^2\sin^2\gamma}\left[-(3\mathrm{K}^2+1)(3-2\kappa^2\sin^2\gamma)-(\mathrm{K}^2+3)\sin^2\gamma\right]\ldots(\text{v})'.$$

$$\begin{aligned}3\mathfrak{a}\frac{d}{d\mathfrak{a}}\Bigg[k^2\mathcal{K}^4\left(\frac{5}{\kappa^2\mathrm{K}^4}+\frac{1}{\mathrm{K}^4}+\frac{2}{\kappa^2\mathrm{K}^2}+\frac{2}{\mathrm{K}^2}+\frac{1}{\kappa^2}+5\right)&\\ +\text{same with small and large interchanged}\Bigg] &= \frac{2k^2\mathcal{K}^4}{\kappa^2\mathrm{K}^4\sin^2\gamma}\left[-(5+2\mathrm{K}^2+\mathrm{K}^4)(3-2\sin^2\gamma)-\kappa^2(1+2\mathrm{K}^2+5\mathrm{K}^4)\sin^2\gamma\right]\\ &\quad+\frac{4k^4\mathcal{K}^2}{\kappa^4\mathrm{K}^2\sin^2\gamma}\Big[-3\,(5+\kappa^2)+(10+\kappa^2-\kappa^4)\sin^2\gamma\\ &\qquad-\mathrm{K}^2\left\{3\,(1+\kappa^2)-(2+\kappa^2-5\kappa^4)\sin^2\gamma\right\}\Big]\;\ldots\;(\text{vi}),\end{aligned}$$

$$\begin{aligned}3\mathfrak{b}\frac{d}{d\mathfrak{b}}\qquad\text{same}\qquad &= \frac{2k^2\mathcal{K}^4}{\kappa^2\mathrm{K}^4\sin^2\gamma}\left[-(5+2\mathrm{K}^2+\mathrm{K}^4)\sin^2\gamma-(1+2\mathrm{K}^2+5\mathrm{K}^4)(3-2\kappa^2\sin^2\gamma)\right]\\ &\quad+\frac{4k^4\mathcal{K}^2}{\kappa^4\mathrm{K}^2\sin^2\gamma}\Big[-3\,(1+\kappa^2)+(2\kappa^4+\kappa^2-5)\sin^2\gamma\\ &\qquad-\mathrm{K}^2\left\{3\,(5\kappa^2+1)-(10\kappa^4+\kappa^2-1)\sin^2\gamma\right\}\Big]\;\ldots\;(\text{vi})'.\end{aligned}$$

On picking out the numerical coefficients of the several terms in $(eE)_2$ as given in (14) or (15), we see that

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}(eE)_2 = \frac{(\frac{4}{3}\pi\rho\mathrm{a}^3)^2\lambda}{(1+\lambda)^2}\left\{\frac{1\,(\text{ii})}{2.5r^3}+\frac{3\,(\text{iii})}{2^3.5.7r^5}+\frac{3\,(\text{v})}{2^2.5^2r^5}+\frac{1\,(\text{iv})}{2^4.3.7r^7}+\frac{9\,(\text{vi})}{2^4.5.7r^7}\right\}.$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}(eE)_2 = \quad .\quad .\quad .\quad .\quad (\text{ii})'\,.\quad .\,(\text{iii})'\,.\quad .\,(\text{v})'\,.\quad .\,(\text{iv})'\,.\quad .\,(\text{vi})'.$$

Observe that $\dfrac{k^2}{\kappa^2\sin^2\gamma} = \dfrac{k^2}{\sin^2\beta} = c^2$, and write

$$\left.\begin{aligned}\tau &= \frac{3}{2^3.7r^2}\frac{\kappa^2\sin^2\gamma}{k^2}(\text{iii})+\frac{3}{2^2.5r^2}\frac{\kappa^2\sin^2\gamma}{k^2}(\text{v})+\frac{5}{2^4.3.7r^4}\frac{\kappa^2\sin^2\gamma}{k^2}(\text{iv})+\frac{9}{2^4.7r^4}\frac{\kappa^2\sin^2\gamma}{k^2}(\text{vi})\\ \sigma &= \quad .\quad .\quad .\quad .\,(\text{iii})'\,.\quad .\quad .\quad .\quad .\,(\text{v})'\quad .\quad .\quad .\quad .\quad .\,(\text{iv})'\,.\quad .\quad .\quad .\quad .\,(\text{vi})'\end{aligned}\right\}\quad (27).$$

Then we have

$$\left.\begin{aligned}3\mathfrak{a}\frac{d}{d\mathfrak{a}}(eE)_2 &= (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[\frac{1}{5r^3}(b^2-2a^2-2c^2)+\frac{1}{5r^3}\cdot\tau c^2\right]\\ 3\mathfrak{b}\frac{d}{d\mathfrak{b}}(eE)_2 &= (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[\frac{1}{5r^3}(a^2-2b^2-2c^2)+\frac{1}{5r^3}\cdot\sigma c^2\right]\end{aligned}\right\}\quad .\quad .\quad (28).$$

The terms in V denoted $(eE)_1$ and (VV) do not contain a, b, c, and their differentials with respect to $\mathfrak{a}$, $\mathfrak{b}$ are zero; also, after omission of the terms in f_i^s, (vv) is reduced to

$$(vv) = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\cdot\tfrac{3}{10}\lambda\psi.$$

Hence

$$3\mathfrak{a}\frac{d}{d\mathfrak{a}}(vv) = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[\tfrac{3}{10}\lambda\left(2a\frac{\partial\psi}{\partial a}-b\frac{\partial\psi}{\partial b}-c\frac{\partial\psi}{\partial c}\right)\right],$$

$$3\mathfrak{b}\frac{d}{d\mathfrak{b}}(vv) = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[\tfrac{3}{10}\lambda\left(2b\frac{\partial\psi}{\partial b}-a\frac{\partial\psi}{\partial a}-c\frac{\partial\psi}{\partial c}\right)\right].$$

Now

$$a\frac{\partial\psi}{\partial a} = -\frac{2}{k}\mathsf{P}_1^1(\nu_0)\,\mathsf{Q}_1^1(\nu_0) = -\frac{2}{k}\mathsf{A}_1^1,$$

$$b\frac{\partial\psi}{\partial b} = -\frac{2}{k}\mathfrak{P}_1^1(\nu_0)\,\mathfrak{Q}_1^1(\nu_0) = -\frac{2}{k}\mathfrak{A}_1^1,$$

$$c\frac{\partial\psi}{\partial c} = -\frac{2}{k}\mathfrak{P}_1(\nu_0)\,\mathfrak{Q}_1(\nu_0) = -\frac{2}{k}\mathfrak{A}_1.$$

Since ψ is homogeneous of degree -1 in a, b, c, the sum of these three is equal to -1, so that

$$\mathsf{A}_1^1+\mathfrak{A}_1^1+\mathfrak{A}_1 = \tfrac{1}{2}k\psi.$$

Therefore

$$\left.\begin{aligned} 3\mathfrak{a}\frac{d}{d\mathfrak{a}}(vv) &= -(\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\cdot\frac{3\lambda}{5k}(3\mathsf{A}_1{}^1-\tfrac{1}{2}k\psi), \\ 3\mathfrak{b}\frac{d}{d\mathfrak{b}}(vv) &= -(\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\cdot\frac{3\lambda}{5k}(3\mathfrak{A}_1{}^1-\tfrac{1}{2}k\psi), \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (29).$$

On adding together (28) and (29), we find

$$3\mathfrak{a}\frac{dV}{d\mathfrak{a}} = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[-\frac{3\lambda}{5k}(3\mathsf{A}_1{}^1-\tfrac{1}{2}k\psi)+\frac{1}{5r^3}(b^2-2a^2-2c^2+\tau c^2)\right],$$

$$3\mathfrak{b}\frac{dV}{d\mathfrak{b}} = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\left[-\frac{3\lambda}{5k}(3\mathfrak{A}_1{}^1-\tfrac{1}{2}k\psi)+\frac{1}{5r^3}(a^2-2b^2-2c^2+\sigma c^2)\right].$$

By means of (i) and (i)′ we find the differentials of the moment of inertia I; they are

$$3\mathfrak{a}\frac{dI}{d\mathfrak{a}} = -\tfrac{4}{3}\pi\rho\mathrm{a}^3\frac{\lambda}{1+\lambda}\cdot\tfrac{2}{5}(b^2+c^2),$$

$$3\mathfrak{b}\frac{dI}{d\mathfrak{b}} = \tfrac{4}{3}\pi\rho\mathrm{a}^3\frac{\lambda}{1+\lambda}\cdot\tfrac{2}{5}(2b^2-c^2).$$

Then, since $\tfrac{1}{2}\omega^2 = \tfrac{4}{3}\pi\rho\mathrm{a}^3\cdot\dfrac{1}{2r^3}(1+\zeta)$,

$$\tfrac{3}{2}\omega^2\mathfrak{a}\frac{dI}{d\mathfrak{a}} = -(\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\cdot\frac{1}{5r^3}(1+\lambda)(1+\zeta)(b^2+c^2),$$

$$\tfrac{3}{2}\omega^2\mathfrak{b}\frac{dI}{d\mathfrak{b}} = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2\frac{\lambda}{(1+\lambda)^2}\cdot\frac{1}{5r^3}(1+\lambda)(1+\zeta)(2b^2-c^2).$$

Now the equations for equilibrium for the parameters $\mathfrak{a}$ and $\mathfrak{b}$ are

$$\frac{dV}{d\mathfrak{a}}+\tfrac{1}{2}\omega^2\frac{dI}{d\mathfrak{a}} = 0, \quad \frac{dV}{d\mathfrak{b}}+\tfrac{1}{2}\omega^2\frac{dI}{d\mathfrak{b}} = 0.$$

Therefore

$$\left.\begin{aligned} -3\lambda(3\mathsf{A}_1{}^1-\tfrac{1}{2}k\psi)+\frac{k}{r^3}[b^2-2a^2-2c^2+\tau c^2-(1+\lambda)(1+\zeta)(b^2+c^2)] &= 0 \\ -3\lambda(3\mathfrak{A}_1{}^1-\tfrac{1}{2}k\psi)+\frac{k}{r^3}[a^2-2b^2+2c^2+\sigma c^2+(1+\lambda)(1+\zeta)(2b^2-c^2)] &= 0 \end{aligned}\right\} \quad . \quad (30).$$

Subtracting the second of these from the first and dividing by 9λ, we have

$$\mathfrak{A}_1{}^1-\mathsf{A}_1{}^1 = \frac{k}{3\lambda r^3}[a^2-b^2+b^2(1+\lambda)(1+\zeta)-\tfrac{1}{3}c^2(\tau-\sigma)] \quad . \quad . \quad . \quad . \quad (31).$$

Since we may write $3\mathsf{A}_1{}^1 - \frac{1}{2}k\psi$ in the form $-(\mathfrak{A}_1{}^1 - \mathsf{A}_1{}^1) - (\mathfrak{A}_1 - \mathsf{A}_1{}^1)$, the first of (30) in combination with (31) gives

$$\mathfrak{A}_1 - \mathsf{A}_1{}^1 = \frac{k}{3\lambda r^3}\left[a^2 + 2c^2 + c^2(1+\lambda)(1+\zeta) - \tfrac{1}{3}c^2(2\tau+\sigma)\right] \quad . \quad . \quad . \quad (32).$$

Referring to the values of τ and σ in (27), I find

$$\begin{aligned}-\tfrac{1}{3}(\tau-\sigma) = {} & \tfrac{3}{14}\frac{k^2\kappa'^2}{r^2\kappa^2}\left[2 - 3(1+\kappa^2)\sin^2\gamma\right] + \tfrac{5}{56}\frac{k^4\kappa'^2}{r^4\kappa^4}\left[4(1+\kappa^2) - (5+6\kappa^2+5\kappa^4)\sin^2\gamma\right] \\ & + \tfrac{3}{10}\frac{\mathcal{K}^2}{r^2\mathrm{K}^2}\left[2\mathrm{K}'^2\cos^2\gamma - \kappa'^2\sin^2\gamma\,(1+3\mathrm{K}^2)\right] \\ & + \tfrac{9}{56}\frac{\mathcal{K}^4}{r^4\mathrm{K}^4}\left[4\mathrm{K}'^2(1+\mathrm{K}^2)\cos^2\gamma - \kappa'^2\sin^2\gamma\,(1+2\mathrm{K}^2+5\mathrm{K}^4)\right] \\ & + \tfrac{9}{28}\frac{k^2\mathcal{K}^2}{r^4\kappa^2\mathrm{K}^2}\left[4(1-\kappa^2\mathrm{K}^2)\cos^2\gamma - \kappa'^2\sin^2\gamma\,(1+\kappa^2+\mathrm{K}^2+5\kappa^2\mathrm{K}^2)\right].\end{aligned}$$

$$\begin{aligned}-\tfrac{1}{3}(2\tau+\sigma) = {} & \tfrac{3}{14}\frac{k^2}{r^2\kappa^2}\left[7+5\kappa^2 - (3+\kappa^2)\sin^2\gamma\right] + \tfrac{5}{56}\frac{k^4}{r^4\kappa^4}\left[11+6\kappa^2+7\kappa^4 - (5+2\kappa^2+\kappa^4)\sin^2\gamma\right] \\ & + \tfrac{3}{10}\frac{\mathcal{K}^2}{r^2\mathrm{K}^2}\left[7+5\mathrm{K}^2 - (3+\mathrm{K}^2)\sin^2\gamma\right] \\ & + \tfrac{9}{56}\frac{\mathcal{K}^4}{r^4\mathrm{K}^4}\left[11+6\mathrm{K}^2+7\mathrm{K}^4 - (5+2\mathrm{K}^2+\mathrm{K}^4)\sin^2\gamma\right] \\ & + \tfrac{9}{28}\frac{k^2\mathcal{K}^2}{r^4\kappa^2\mathrm{K}^2}\left[11+3\kappa^2+3\mathrm{K}^2+7\kappa^2\mathrm{K}^2 - (5+\kappa^2+\mathrm{K}^2+\kappa^2\mathrm{K}^2)\sin^2\gamma\right] \quad . \quad . \quad . \quad (33).\end{aligned}$$

In all the cases which we shall have to consider the first of these expressions is small compared with the second, because κ is nearly equal to unity and κ' small, and because $\cos^2\gamma$ is also rather small.

Now let

$$\left.\begin{aligned}\epsilon &= -\tfrac{1}{3}(\tau-\sigma) + \zeta(1+\lambda)\cos^2\beta \\ \eta &= -\tfrac{1}{3}(2\tau+\sigma) + \zeta(1+\lambda)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33\ bis).$$

Then, since $a = c\cos\gamma$, $b = c\cos\beta$, the equations (31) and (32) become

$$\left.\begin{aligned}\mathfrak{A}_1{}^1 - \mathsf{A}_1{}^1 &= \frac{kc^2}{3\lambda r^3}(\cos^2\gamma + \lambda\cos^2\beta + \epsilon) \\ \mathfrak{A}_1 - \mathsf{A}_1{}^1 &= \frac{kc^2}{3\lambda r^3}(3+\lambda+\cos^2\gamma+\eta)\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34).$$

Eliminating $kc^2/3\lambda r^3$, we have

$$(\mathfrak{A}_1 - \mathsf{A}_1{}^1)(\cos^2\gamma + \lambda\cos^2\beta + \epsilon) = (\mathfrak{A}_1{}^1 - \mathsf{A}_1{}^1)(3+\lambda+\cos^2\gamma+\eta) \quad . \quad . \quad (35).$$

This is the equation to be satisfied by the axes of the ellipsoid. If we treat ϵ and η as zero, it is the same as that found by ROCHE.*

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* The form of this equation is so unlike ROCHE'S, that it may be worth while to prove the identity of the two.

ROCHE writes his equations in the form

$$\frac{st(t-s)}{(3+\lambda)t-\lambda s}\int_0^\infty \frac{u\,du}{(1+su)(1+tu)R} = \frac{s(1-s)}{s+3+\lambda}\int_0^\infty \frac{u\,du}{(1+su)(1+u)R} = \frac{t(1-t)}{t+\lambda}\int_0^\infty \frac{u\,du}{(1+u)(1+tu)R},$$

where $R^2 = (1+u)(1+su)(1+tu)$, and s is the square of the ratio of the least to the greatest axis, and t the square of the ratio of the least to the mean axis.

In my notation

$$s = \frac{a^2}{c^2} = \cos^2\gamma, \quad t = \frac{a^2}{b^2} = \frac{\cos^2\gamma}{\cos^2\beta}.$$

If we write $us+1 = \dfrac{\sin^2\gamma}{\sin^2\psi}$, and change the independent variable from u to ψ, we find

$$\left.\begin{aligned}
\text{ROCHE'S first integral} &= \frac{2\cos^3\beta}{\sin^5\gamma\cos^3\gamma}\int_0^\gamma \frac{\sin^2\psi(\sin^2\gamma-\sin^2\psi)}{\Delta^3}\,d\psi \\
\text{,, second ,,} &= \frac{2\cos\beta}{\sin^5\gamma\cos\gamma}\int_0^\gamma \frac{\sin^2\psi(\sin^2\gamma-\sin^2\psi)}{\cos^2\psi\Delta}\,d\psi \\
\text{,, third ,,} &= \frac{2\cos^3\beta}{\sin^5\gamma\cos\gamma}\int_0^\gamma \frac{\sin^2\psi(\sin^2\gamma-\sin^2\psi)}{\cos^2\psi\,\Delta^3}\,d\psi
\end{aligned}\right\} \quad \ldots\ldots \quad (\text{A}),$$

where $\Delta^2 = 1-\kappa^2\sin^2\psi$.

The coefficients are

$$\left.\begin{aligned}
\frac{st(t-s)}{(3+\lambda)t-\lambda s} &= \frac{\cos^4\gamma\sin^2\beta}{\cos^2\beta\,[(3+\lambda)-\lambda\cos^2\beta]} \\
\frac{s(1-s)}{s+3+\lambda} &= \frac{\sin^2\gamma\cos^2\gamma}{3+\lambda+\cos^2\gamma} \\
\frac{t(1-t)}{t+\lambda} &= \frac{\kappa'^2\sin^2\gamma\cos^2\gamma}{\cos^2\beta(\cos^2\gamma+\lambda\cos^2\beta)}
\end{aligned}\right\} \quad \ldots\ldots\ldots\ldots \quad (\text{B}).$$

Then ROCHE'S equations are equivalent to

1st of (A) × 1st of (B) = 2nd of (A) × 2nd of (B) = 3rd of (A) × 3rd of (B).

But the two equations are not independent, and I will only pursue the consideration of the form involving the 2nd and 3rd of (A) and (B).

Now

$$\frac{\sin^2\psi(\sin^2\gamma-\sin^2\psi)}{\cos^2\psi\,\Delta} = \frac{\sin^2\psi}{\Delta} - \cos^2\gamma\frac{\tan^2\psi}{\Delta},$$

$$\frac{\sin^2\psi(\sin^2\gamma-\sin^2\psi)}{\cos^2\psi\,\Delta^3} = \frac{\cos^2\beta}{\kappa'^2}\frac{\sin^2\psi}{\Delta^3} - \frac{\cos^2\gamma}{\kappa'^2}\frac{\tan^2\psi}{\Delta},$$

and I have proved in (25) of the "Pear-shaped figure, &c." that

$$\mathfrak{A}_1 = \mathfrak{P}_1\mathfrak{Q}_1 = \frac{\kappa}{\sin^2\gamma}\int_0^\gamma \frac{\sin^2\psi}{\Delta}\,d\psi,$$

$$\mathsf{A}_1{}^1 = \mathsf{P}_1{}^1\mathsf{Q}_1{}^1 = \frac{\kappa\cos^2\gamma}{\sin^2\gamma}\int_0^\gamma \frac{\tan^2\psi}{\Delta}\,d\psi,$$

$$\mathfrak{A}_1{}^1 = \mathfrak{P}_1{}^1\mathfrak{Q}_1{}^1 = \frac{\kappa\cos^2\beta}{\sin^2\gamma}\int_0^\gamma \frac{\sin^2\psi}{\Delta^3}\,d\psi.$$

It is possible to express this equation in terms of elliptic integrals and to use LEGENDRE'S tables for finding the solution, but the method is very tedious, and after finding a few solutions in that way I abandoned it. It may, however, be worth while to mention that

$$\mathfrak{A}_1-\mathsf{A}_1{}^1 = \frac{\kappa}{\sin^2\gamma}\left[-\frac{1}{\kappa'^2}\sin\gamma\cos\gamma\cos\beta+\frac{F}{\kappa^2}+\frac{\cos^2\beta-2\kappa'^2}{\kappa^2\kappa'^2}E\right],$$

$$\mathfrak{A}_1{}^1-\mathsf{A}_1{}^1 = \frac{\kappa}{\sin^2\gamma}\left[-\frac{2}{\kappa'^2}\sin\gamma\cos\gamma\cos\beta-\frac{\cos^2\beta}{\kappa^2}F+\frac{2\cos^2\beta-\kappa'^2}{\kappa^2\kappa'^2}E\right],$$

where

$$F=\int_0^\gamma\frac{d\psi}{\sqrt{(1-\kappa^2\sin^2\psi)}}, \quad E=\int_0^\gamma\sqrt{(1-\kappa^2\sin^2\psi)}\,d\psi.$$

When the forms of the ellipsoids have been determined, the radius vector becomes determinable from either of the equations (34).

The conditions that the internal potential of an ellipsoid satisfies POISSON'S equation and that ψ is homogeneous in a, b, c of degree -1, give the two following equations :—

$$\frac{\mathsf{A}_1{}^1}{a^2}+\frac{\mathfrak{A}_1{}^1}{b^2}+\frac{\mathfrak{A}_1}{c^2}-\frac{k}{abc} = 0,$$

$$\mathsf{A}_1{}^1+\mathfrak{A}_1{}^1+\mathfrak{A}_1-\tfrac{1}{2}k\psi = 0.$$

Our two equations for $1/r^3$ may be written

$$\mathsf{A}_1{}^1-\mathfrak{A}_1{}^1 \qquad +\frac{k}{3\lambda r^3}(a^2+b^2\lambda+c^2\epsilon) = 0,$$

$$\mathsf{A}_1{}^1 \qquad -\mathfrak{A}_1+\frac{k}{3\lambda r^3}[(3+\lambda)c^2+a^2+c^2\eta] = 0.$$

These four equations afford a determinant by which $\mathsf{A}_1{}^1$, $\mathfrak{A}_1{}^1$, $\mathfrak{A}_1$ may be eliminated. On reduction we find

$$\frac{1}{3\lambda r^3} = \frac{\tfrac{1}{2}\psi-\dfrac{3/abc}{1/a^2+1/b^2+1/c^2}}{3c^2-a^2+\lambda(b^2+c^2)+c^2(\eta+\epsilon)-\dfrac{6\left(1+\lambda+\frac{1}{2}\eta+\frac{1}{2}c^2\epsilon/b^2\right)}{1/a^2+1/b^2+1/c^2}}.$$

Therefore ROCHE'S second integral is equal to $\dfrac{2\cos\beta}{\kappa\sin^3\gamma\cos\gamma}(\mathfrak{A}_1-\mathsf{A}_1{}^1)$, and his third integral is equal to $\dfrac{2\cos^3\beta}{\kappa\kappa'^2\sin^3\gamma\cos\gamma}(\mathfrak{A}_1{}^1-\mathsf{A}_1{}^1)$.

Using these transformations of the second and third of (A), and dropping redundant factors, we get

$$(\cos^2\gamma+\lambda\cos^2\beta)(\mathfrak{A}_1-\mathsf{A}_1{}^1) = (3+\lambda+\cos^2\gamma)(\mathfrak{A}_1{}^1-\mathsf{A}_1{}^1).$$

This agrees with the result in the text when ϵ and η are neglected.

On putting $a = c\cos\gamma$, $b = c\cos\beta$, and noting that $\psi = \dfrac{2F}{c\sin\gamma}$ and that $\dfrac{1+\lambda}{\lambda}c^3\cos\gamma\cos\beta = \mathrm{a}^3$, I find that

$$\frac{\mathrm{a}^3}{r^3} = \frac{\frac{3}{2}\left[2F\cot\gamma\cos\beta - \dfrac{6}{1+\sec^2\gamma+\sec^2\beta}\right]}{\dfrac{3-\cos^2\gamma+\lambda(1+\cos^2\beta)}{1+\lambda} - \dfrac{6}{1+\sec^2\gamma+\sec^2\beta}+\delta} \quad . \quad . \quad . \quad (36),^*$$

where

$$\delta = \frac{1}{1+\lambda}\left[\eta+\epsilon-\frac{3(\eta+\epsilon\sec^2\beta)}{1+\sec^2\gamma+\sec^2\beta}\right].$$

However, this is not practically the most convenient form from which to compute the distance between the two ellipsoids.

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[*] It is by no means obvious how this formula is consistent with results which we know by other means to be true. In the case when $\lambda = \infty$ we have a liquid planet rotating with the same angular velocity as an infinitely small satellite revolving in a circular orbit in its equator.

Let us first consider the value of ζ. In the present case the semi-axes A, B, C pertain to the infinitely small satellite, and are therefore negligible compared with terms in a, b, c. Since the axis denoted by c is that coincident with the satellite's radius vector, and since the equatorial plane of the planet must have a circular section, we have $c = b$.

But since $b = c\cos\beta$, it follows that $\beta = 0$ or $\kappa\sin\gamma = 0$. Now γ does not vanish for $a = c\cos\gamma$, and a is the polar semi-radius of the planet; therefore $\kappa = 0$.

If we consider the formula (24) for ζ, expressing, however, the several terms in the form of (15), we see that for $\lambda = \infty$

$$\zeta = \frac{3}{10r^2}(c^2-a^2) + \frac{3}{56r^4}\cdot 3(c^2-a^2)^2 + \frac{1}{48r^6}\cdot 5(c^2-a^2)^3 \ldots,$$

whence

$$\zeta = \frac{3c^2}{10r^2}\sin^2\gamma + \frac{9c^4}{56r^4}\sin^4\gamma + \frac{5c^6}{48r^6}\sin^6\gamma \ldots \quad . \quad . \quad . \quad (a).$$

The factor of correction to KEPLER'S law of periodic times for a small satellite revolving about an oblate planet, whose equatorial radius is c and whose eccentricity of figure is $\sin\gamma$, is $1+\zeta$, where ζ is expressed by the above series (a).

Now considering the formula (33 *bis*), we see that for $\lambda = \infty$ and $\beta = 0$

$$\frac{\epsilon}{1+\lambda} = \zeta\cos^2\beta = \zeta; \quad \frac{\eta}{1+\lambda} = \zeta.$$

In (36) we therefore have

$$\delta = \frac{1}{1+\lambda}\left[\eta+\epsilon-\frac{3(\eta+\epsilon\sec^2\beta)}{1+\sec^2\beta+\sec^2\gamma}\right] = 2\zeta\left[1-\frac{3}{3+\tan^2\gamma}\right] = \frac{2\zeta\tan^2\gamma}{3+\tan^2\gamma}.$$

When $\kappa = 0$, the elliptic integral F is equal to γ; thus (36) becomes

$$\frac{\mathrm{a}^3}{r^3} = \frac{\frac{3}{2}\left[2\gamma\cot\gamma - \dfrac{6}{3+\tan^2\gamma}\right]}{2-\dfrac{6}{3+\tan^2\gamma}+\dfrac{2\zeta\tan^2\gamma}{3+\tan^2\gamma}}.$$

§ 11. *Solution of the Equations.*

In all the ellipsoids of which we shall have to find the axes, it happens that $\kappa'^2 \tan^2 \gamma$ is fairly small compared with unity. Hence it is possible to expand Δ in powers of that quantity.

We have

$$\Delta^2 = 1-\kappa^2 \sin^2 \gamma = \cos^2 \gamma \, (1+\kappa'^2 \tan^2 \gamma),$$

and

$$\frac{1}{\Delta} = \frac{1}{\cos \gamma} \left[1-\tfrac{1}{2}\kappa'^2 \tan^2 \gamma + \tfrac{1\cdot 3}{2\cdot 4}\kappa'^4 \tan^4 \gamma - \ldots\right],$$

$$\frac{1}{\Delta^3} = \frac{1}{\cos^3 \gamma} \left[1-\tfrac{3}{2}\kappa'^2 \tan^2 \gamma + \tfrac{3\cdot 5}{2\cdot 4}\kappa'^4 \tan^4 \gamma - \ldots\right].$$

From this we easily obtain

$$\frac{\omega^2}{2\pi\rho} = \tfrac{2}{3}(1+\zeta)\frac{\mathrm{a}^3}{r^3} = \cot^3 \gamma \left[\gamma\,(3+\tan^2 \gamma) - 3 \tan \gamma\right].$$

This is the well-known formula for the angular velocity of MACLAURIN'S ellipsoid.

It should be remarked that (35) is identically satisfied by $\lambda = \infty$, $\kappa = 0$, for when we use the above values of ϵ and η, the equation becomes divisible by $1+\zeta$.

Since ζ is a symmetrical function of a, b, c and A, B, C, it follows that ζ is the same in form for λ and for $1/\lambda$. Therefore when we consider the case of $\lambda = 0$, the formula (a) gives the required result, but c and γ refer to the large body which is throughout most of this paper indicated by capital letters.

Thus for $\lambda = 0$,

$$\zeta = \tfrac{3}{10}\frac{C^2}{r^2}\sin^2\Gamma + \tfrac{9}{56}\left(\frac{C^2}{r^2}\sin^2\Gamma\right)^2 + \tfrac{5}{48}\left(\frac{C^2}{r^2}\sin^2\Gamma\right)^3 \ldots$$

$$= \tfrac{3}{10}\frac{\mathrm{a}^2}{r^2}\frac{\sin^2\Gamma}{\cos^{2/3}\Gamma} + \tfrac{9}{56}\frac{\mathrm{a}^4}{r^4}\left(\frac{\sin^2\Gamma}{\cos^{2/3}\Gamma}\right)^2 + \tfrac{5}{48}\frac{\mathrm{a}^6}{r^6}\left(\frac{\sin^2\Gamma}{\cos^{2/3}\Gamma}\right)^3 \ldots$$

In the case of $\lambda = 0$, k vanishes; K also vanishes and so also does the angle B. Hence we have

$$\epsilon = \zeta \cos^2 \beta, \quad \eta = \zeta.$$

With these values, equation (35) becomes

$$(\mathfrak{A}_1 - \mathsf{A}_1{}^1)\left[\cos^2\gamma + (\lambda+\zeta)\cos^2\beta\right] = (\mathfrak{A}_1{}^1 - \mathsf{A}_1{}^1)\left[3 + (\lambda+\zeta) + \cos^2\gamma\right].$$

Hence ζ plays the part of an augmentation to λ.

With $\lambda = 0$ the equation assumes the form

$$(\mathfrak{A}_1 - \mathsf{A}_1{}^1)(\cos^2\gamma + \zeta\cos^2\beta) = (\mathfrak{A}_1{}^1 - \mathsf{A}_1{}^1)(3+\zeta+\cos^2\gamma) \quad \ldots \ldots \ldots \quad (b).$$

It follows therefore that an infinitesimal satellite revolving about an oblate planet, whose rotation is the same as the revolution of the satellite, is very nearly identical in form with a small but finite satellite whose mass is a fraction of a *spherical* planet expressed by ζ. This curious conclusion follows from the fact that if we take equation (35) and put ϵ and η zero (which corresponds to a spherical planet and small satellite), we get exactly the equation (b) just found, only with λ in place of ζ.

Now from (25) of the "Pear-shaped figure,"

$$\mathfrak{A}_1 = \frac{\kappa}{\sin^2\gamma}\int_0^\gamma \frac{\sin^2\gamma}{\Delta}\,d\gamma, \quad \mathbf{A}_1{}^1 = \frac{\kappa\cos^2\gamma}{\sin^2\gamma}\int_0^\gamma \frac{\tan^2\gamma}{\Delta}\,d\gamma, \quad \mathfrak{A}_1{}^1 = \frac{\kappa\cos^2\beta}{\sin^2\gamma}\int_0^\gamma \frac{\sin^2\gamma}{\Delta^3}\,d\gamma.$$

When the Δ's under the integral signs are expanded, all the terms of the series involve integrals of one of two types. If we write

$$\Omega = \frac{1}{\sin\gamma}\log_e\frac{1+\sin\gamma}{\cos\gamma},$$

the types are

$$\int_0^\gamma \frac{\sin^{2n}\gamma}{\cos^{2n-1}\gamma}\,d\gamma = \sin\gamma\left[\frac{1}{2n-2}\tan^{2n-2}\gamma - \frac{2n-1}{(2n-2)(2n-4)}\tan^{2n-4}\gamma + \ldots \right.$$
$$\left. +(-)^n\frac{(2n-1)(2n-3)\ldots 5}{(2n-2)(2n-4)\ldots 2}\tan^2\gamma + (-)^{n+1}\frac{(2n-1)\ldots 3}{(2n-2)\ldots 2}(\Omega-1)\right],$$

$$\int_0^\gamma \frac{\sin^{2n}\gamma}{\cos^{2n+1}\gamma}\,d\gamma = \sin\gamma\left[\frac{1}{2n}\tan^{2n}\gamma - \frac{1}{2n(2n-2)}\tan^{2n-2}\gamma + \frac{2n-1}{2n(2n-2)(2n-4)}\tan^{2n-4}\gamma - \ldots \right.$$
$$\left. -(-)^n\frac{(2n-1)(2n-3)\ldots 5}{2n(2n-2)\ldots 2}\tan^2\gamma - (-)^{n+1}\frac{(2n-1)\ldots 3}{2n(2n-2)\ldots 2}(\Omega-1)\right].$$

As it is not quite obvious what interpretation is to be put on these formulæ for the smaller values of n, I may mention that when $n = 0, 1, 2$ respectively, the first integral is $\sin\gamma$; $\sin\gamma\,(\Omega-1)$; $\sin\gamma\,[\frac{1}{2}\tan^2\gamma - \frac{3}{2}(\Omega-1)]$, and the second is $\sin\gamma\,\Omega$; $\sin\gamma\,[\frac{1}{2}\tan^2\gamma - \frac{1}{2}(\Omega-1)]$; $\sin\gamma\,[\frac{1}{4}\tan^4\gamma - \frac{1}{4.2}\tan^2\gamma + \frac{3}{4.2}(\Omega-1)]$. For larger values of n the interpretation is obvious.

If we use these integrals and write

$$\left.\begin{aligned} \frac{\sin\gamma}{\kappa}(\mathfrak{A}_1{}^1 - \mathbf{A}_1{}^1) &= \kappa'^2\,[\sigma_0 - \sigma_1\kappa'^2 + \sigma_2\kappa'^4 - \sigma_3\kappa'^6\ldots] \\ \frac{\sin\gamma}{\kappa}(\mathfrak{A}_1 - \mathbf{A}_1{}^1) &= \tau_0 - \tau_1\kappa'^2 + \tau_2\kappa'^4 - \tau_3\kappa'^6\ldots \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (37),$$

we find

$$\sigma_0 = \tfrac{1}{8}[2\tan^2\gamma + 3 - (3+\sin^2\gamma)\,\Omega]$$
$$\sigma_1 = \tfrac{3}{32}[\tfrac{4}{3}\tan^4\gamma - \tfrac{8}{3}\tan^2\gamma - 5 + (5+\sin^2\gamma)\,\Omega]$$
$$\sigma_2 = \tfrac{75}{1024}[\tfrac{16}{15}\tan^6\gamma - \tfrac{8}{5}\tan^4\gamma + \tfrac{10}{3}\tan^2\gamma + 7 - (7+\sin^2\gamma)\,\Omega]$$
$$\sigma_3 = \tfrac{245}{4096}[\tfrac{32}{35}\tan^8\gamma - \tfrac{128}{105}\tan^6\gamma + \tfrac{28}{15}\tan^4\gamma - 4\tan^2\gamma - 9 + (9+\sin^2\gamma)\,\Omega]$$
$$\tau_0 = \tfrac{1}{2}[-3 + (3-\sin^2\gamma)\,\Omega]$$
$$\tau_1 = \tfrac{3}{16}[\tfrac{2}{3}\tan^2\gamma + 5 - (5-\sin^2\gamma)\,\Omega]$$
$$\tau_2 = \tfrac{15}{128}[\tfrac{4}{15}\tan^4\gamma - \tfrac{4}{3}\tan^2\gamma - 7 + (7-\sin^2\gamma)\,\Omega]$$
$$\tau_3 = \tfrac{175}{2048}[\tfrac{16}{105}\tan^6\gamma - \tfrac{8}{15}\tan^4\gamma + 2\tan^2\gamma + 9 - (9-\sin^2\gamma)\,\Omega]$$
$$\tau_4 = \tfrac{5.3^2.7^2}{2^{15}}[\tfrac{32}{315}\tan^8\gamma - \tfrac{32}{105}\tan^6\gamma + \tfrac{4}{5}\tan^4\gamma - \tfrac{4}{3}\tan^2\gamma - 11 + (11-\sin^2\gamma)\Omega]. \quad (38).$$

It would not be difficult to find the general expressions for these functions, but it does not seem worth while to do so.

The equation (35) for determining the form of the ellipsoid involves the factor $\cos^2\gamma+\lambda\cos^2\beta+\epsilon$; if we write

$$M=\frac{\lambda\sin^2\gamma}{(1+\lambda)\cos^2\gamma+\epsilon},$$

this factor may be written in the form $[(1+\lambda)\cos^2\gamma+\epsilon][1+M\kappa'^2]$. Hence the equation (35) may be written

$$[\tau_0-\tau_1\kappa'^2+\tau_2\kappa'^4-\tau_3\kappa'^6\ldots][(1+\lambda)\cos^2\gamma+\epsilon][1+M\kappa'^2]$$
$$=\kappa'^2[\sigma_0-\sigma_1\kappa'^2+\sigma_2\kappa'^4-\sigma_3\kappa'^6\ldots][3+\lambda+\cos^2\gamma+\eta].$$

If now we put

$$v_0=\frac{\tau_0}{\sigma_0},\quad v_1=\frac{\sigma_1}{\sigma_0}-\frac{\tau_1}{\tau_0},\quad v_2=\frac{\sigma_2}{\sigma_0}-\frac{\tau_2}{\tau_0}-\frac{\sigma_1}{\sigma_0}v_1,\quad v_3=\frac{\sigma_3}{\sigma_0}-\frac{\tau_3}{\tau_0}-\frac{\sigma_1}{\sigma_0}v_2-\frac{\sigma_2}{\sigma_0}v_1,$$

we have

$$\frac{\tau_0-\tau_1\kappa'^2+\tau_2\kappa'^4\ldots}{\sigma_0-\sigma_1\kappa'^2+\sigma_2\kappa'^4\ldots}=v_0[1+v_1\kappa'^2-v_2\kappa'^4+v_3\kappa'^6-\ldots].$$

Hence our equation may be written

$$\frac{v_0[(1+\lambda)\cos^2\gamma+\epsilon]}{3+\lambda+\cos^2\gamma+\eta}(1+v_1\kappa'^2-v_2\kappa'^4+v_3\kappa'^6\ldots)(1+M\kappa'^2)=\kappa'^2.$$

Whence on writing

$$L=\frac{3+\lambda+\cos^2\gamma+\eta}{(1+\lambda)\cos^2\gamma+\epsilon}$$

$$\kappa'^2=\frac{1+(Mv_1-v_2)\kappa'^4-(Mv_2-v_3)\kappa'^6\ldots}{L/v_0-M-v_1}\quad\ldots\ldots\quad(39).$$

The determination of L for given value of γ involves that of η and ϵ, and these can only be found from an approximate preliminary solution of the whole problem. But when L is known approximately, the solution of (39) is very simple, for we first neglect the terms in κ'^4 and κ'^6 on the right-hand side, and so determine a first approximation to κ'. As a fact I have not included the term in κ'^6 in my computations, because it would not make so much as 1′ difference in the value of $\cos^{-1}\kappa'$.

For ROCHE's problem when ϵ and η are neglected the solution is very short, but when these terms are included the computation is laborious.

We now turn to the determination of the radius vector.

We have

$$\mathfrak{A}_1-\mathbf{A}^1{}_1=\frac{kc^2}{3\lambda r^3}(3+\lambda+\cos^2\gamma+\eta).$$

Since $c^2=\dfrac{k^2}{\sin^2\beta}$ and $\dfrac{k^3\cos\gamma\cos\beta}{\sin^3\beta}=\dfrac{\lambda a^3}{1+\lambda}$, we have

$$\frac{kc^2}{3\lambda r^3}=\frac{1}{3(1+\lambda)}\frac{\kappa\sin\gamma}{\cos\beta\cos\gamma}\cdot\frac{a^3}{r^3}.$$

Therefore

$$\frac{\kappa}{\sin\gamma}(\tau_0-\tau_1\kappa'^2+\ldots) = \frac{\kappa\sin\gamma}{3(1+\lambda)\cos\beta\cos\gamma}\frac{\mathrm{a}^3}{r^3}(3+\lambda+\cos^2\gamma+\eta).$$

Whence

$$\frac{\mathrm{a}^3}{r^3} = 3(1+\lambda)\frac{\cos\beta\cos\gamma}{\sin^2\gamma}\frac{\tau_0-\tau_1\kappa'^2+\tau_2\kappa'^4-\tau_3\kappa'^6\ldots}{3+\lambda+\cos^2\gamma+\eta} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (40).$$

Thus a table of values of τ_0, τ_1, τ_2, τ_3 enables us to compute r for a given value of γ, when κ' has been found.

In the following tables the v's and τ's were computed for the even degrees of γ and interpolated for the odd degrees. These functions are found as the differences between large numbers, and therefore great care would be required to determine them

TABLE of Auxiliary Functions.

γ.	Log v_0.	v_1.	Log v_1.	Log v_2.	Log v_3.	τ_0.	Log τ_1.	Log τ_2.	Log τ_3.
30°	9·94493	0·14279	9·15470	7·9576	7·15	0·010592	6·85440	5·9805	5·222
31	9·94085	0·15461	9·18925	8·0264	7·25	0·012124	6·94587	6·1063	5·378
32	9·93661	0·16722	9·22329	8·0941	7·36	0·013824	7·03507	6·2288	5·533
33	9·93222	0·18065	9·25684	8·1607	7·47	0·015702	7·12194	6·3478	5·685
34	9·92764	0·19493	9·28988	8·2263	7·58	0·017774	7·20666	6·4639	5·834
35	9·92285	0·21006	9·32234	8·2906	7·67	0·020052	7·28937	6·5780	5·979
36	9·91786	0·22613	9·35436	8·3541	7·76	0·022554	7·37022	6·6899	6·122
37	9·91269	0·24327	9·38608	8·4173	7·87	0·025294	7·44939	6·7994	6·262
38	9·90731	0·26150	9·41747	8·4800	7·97	0·028290	7·52697	6·9069	6·400
39	9·90167	0·28091	9·44857	8·5418	8·06	0·031559	7·60306	7·0127	6·536
40	9·89578	0·30160	9·47943	8·6031	8·14	0·035121	7·67777	7·1167	6·669
41	9·88965	0·32368	9·51011	8·6646	8·23	0·038994	7·75120	7·2192	6·802
42	9·88327	0·34724	9·54063	8·7259	8·32	0·043203	7·82342	7·3202	6·932
43	9·87665	0·37244	9·57105	8·7869	8·42	0·047768	7·89452	7·4200	7·061
44	9·86974	0·39937	9·60138	8·8476	8·51	0·052713	7·96459	7·5186	7·189
45	9·86257	0·42823	9·63168	8·9081	8·60	0·058064	8·03371	7·6162	7·316
46	9·85509	0·45917	9·66197	8·9685	8·69	0·063847	8·10195	7·7128	7·442
47	9·84729	0·49239	9·69231	9·0290	8·79	0·070093	8·16939	7·8087	7·567
48	9·83915	0·52812	9·72274	9·0896	8·87	0·076830	8·23608	7·9036	7·691
49	9·83069	0·56656	9·75325	9·1505	8·96	0·084093	8·30210	7·9981	7·814
50	9·82187	0·60804	9·78393	9·2117	9·05	0·091916	8·36752	8·0920	7·938
51	9·81263	0·65278	9·81477	9·2733	9·15	0·100336	8·43241	8·1855	8·061
52	9·80300	0·70121	9·84585	9·3353	9·24	0·109394	8·49682	8·2786	8·183
53	9·79298	0·75372	9·87721	9·3976	9·33	0·119134	8·56082	8·3716	8·306
54	9·78252	0·81075	9·90889	9·4606	9·43	0·129601	8·62447	8·4643	8·429
55	9·77159	0·87288	9·94095	9·5245	9·52	0·140845	8·68785	8·5570	8·552
56	9·76016	0·94064	9·97342	9·5893	9·62	0·152919	8·75103	8·6500	8·676
57	9·74819	1·01471	·00634	9·6550	9·72	0·165883	8·81407	8·7431	8·801
58	9·73565	1·09590	·03977	9·7216	9·82	0·179801	8·87703	8·8367	8·926
59	9·72252	1·18517	·07378	9·7893	9·92	0·194740	8·93999	8·9306	9·052
60	9·70874	1·28362	·10844	9·8582	·02	0·210779	9·00303	9·0252	9·179
61	9·69426	1·39268	·14385	9·9287	·13	0·227997	9·06626	9·1206	9·308
62	9·67910	1·51349	·17998	·0006	·24	0·246485	9·12966	9·2168	9·439
63	9·66319	1·6480	·21696	·0743	·36	0·266343	9·19331	9·3140	9·572

with a very high degree of accuracy. The differences of the tabulated numbers do not run with perfect smoothness, showing that there are residual errors of one or two units in the last place of decimals. The accuracy is however amply sufficient for the end in view, and it would have been wasteful to spend more time over the computations.

§ 12. *Determination of the Form of the Second Ellipsoid.*

The parameters Γ and K determine the form of the second ellipsoid in the same way that γ and κ determine the first. It is obvious that a/r is determinable in two ways, and therefore any given value of γ must correspond to a certain definite value of Γ. The fitting together of the two solutions can only be effected with accuracy by interpolation, but it would be so enormously laborious to find by mere conjecture the region in which to begin calculating with assumed values of Γ, that an approximate solution of the problem becomes a practical necessity.

After various trials I find that on neglecting ϵ and η and writing

$$\chi = \frac{\sin^2\gamma}{7(3+\lambda+\cos^2\gamma)}$$

the solution for κ' may be written approximately in the form

$$\kappa'^2 = \frac{(1+\lambda)\cos^2\gamma}{3+\lambda+\cos^2\gamma}\,[1-(9-7\lambda)\,\chi-(111+228\lambda-49\lambda^2)\,\chi^2$$
$$-\tfrac{1}{11}(7875+28185\lambda+42333\lambda^2-3773\lambda^3)\,\chi^3\ldots] \quad . \quad . \quad (41).$$

If ϵ were added to the numerator of the factor outside the bracket, and η to the denominator, this formula would give nearly as good results as the more accurate method of the last section.

Also I find

$$\frac{\mathrm{a}^3}{r^3} = \frac{\frac{2}{5}(1+\lambda)\cos\beta\cos\gamma\sin^2\gamma}{3+\lambda+\cos^2\gamma}\,[1+\tfrac{9}{2}(5+\lambda)\,\chi+\tfrac{1}{8}(3055+1718\lambda+175\lambda^2)\,\chi^2$$
$$+\frac{1}{2^4\cdot 3\cdot 11}(3533389+3222607\lambda+1021479\lambda^2+60025\lambda^3)\,\chi^3+\ldots] \quad . \quad . \quad (42).$$

In order to obtain the desired approximation, it is necessary to express a^3/r^3 by a series which can be inverted; but this is not possible in the form just given, because $\cos\beta$ depends on κ and therefore involves χ. I find then by means of the above series for κ'^2 that

$$\cos\beta\cos\gamma = 1-\tfrac{7}{2}(7+\lambda)\,\chi+\tfrac{7}{8}(69-106\lambda-7\lambda^2)\,\chi^2+\tfrac{7}{16}(253+753\lambda-1901\lambda^2-49\lambda^3)\,\chi^3\ldots$$

On introducing this in the above formula for a^3/r^3, I find

$$\frac{\mathrm{a}^3}{r^3} = \tfrac{14}{5}(1+\lambda)\,\chi\left[1-(2-\lambda)\,\chi-(109+67\lambda+0\lambda^2)\,\chi^2 \right.$$
$$\left. -\frac{1}{2^2.\,3.\,11}\,(157712+261395\lambda+97656\lambda^2+1568\lambda^3)\,\chi^3\ldots\right].$$

On writing

$$\alpha = \tfrac{5}{14}\cdot\frac{1}{1+\lambda}\,\frac{\mathrm{a}^3}{r^3},$$

and inverting the series we find

$$\chi = \alpha+(2-\lambda)\,\alpha^2+(117+59\lambda+2\lambda^2)\,\alpha^3$$
$$+\frac{1}{2^2.\,3.\,11}\,(306872+269975\lambda+5739\lambda^2+908\lambda^3)\,\alpha^4\ldots \quad . \quad . \quad (43).$$

This series expresses a function of γ in series proceeding by powers of a^3/r^3, and a similar series must also connect a function of Γ with the radius vector, so as to determine the figure of the second ellipsoid appropriately. This second series may be written down by symmetry.

Since λ must now be replaced by $1/\lambda$, the function corresponding to α is $\tfrac{5}{14}\dfrac{\lambda}{1+\lambda}\dfrac{\mathrm{a}^3}{r^3}$ or $\lambda\alpha$, and the function corresponding to χ is $\dfrac{\lambda\sin^2\Gamma}{7\left[(3+\cos^2\Gamma)\,\lambda+1\right]}$.

If then we write

$$X = \frac{\sin^2\Gamma}{7\left[(3+\cos^2\Gamma)\,\lambda+1\right]},$$

the symmetrical series for the other ellipsoid is

$$X = \alpha+(2\lambda-1)\,\alpha^2+(117\lambda^2+59\lambda+2\lambda^2)\,\alpha^3$$
$$+\frac{1}{2^2.\,3.\,11}\,(306872\lambda^3+269975\lambda^2+5739\lambda^3+908)\alpha^4\ldots$$

Now α is easily computed for the first ellipsoid, and then X is computed by the series. Thus we have

$$\sin^2\Gamma = \frac{(4\lambda+1)\,X}{\lambda X+\frac{1}{7}}.$$

We obtain in this way a fairly accurate value of Γ corresponding to the value of γ which determines the first ellipsoid. We can then compute K' by the method of the last section. We may thus obtain a good idea of the values of Γ and K with which it is necessary to work in order to obtain the final solution.

§ 13. *The Equilibrium of Two Ellipsoids joined by a Weightless Pipe.*

In § 3 the problem is considered of the equilibrium of two masses of liquid, each constrainedly spherical, when joined by a pipe without weight. It was shown that the condition determining the ratio of the masses for given radius vector is expressed by a certain equation which was written $f(\mathrm{a}/r)' = 0$. Further, it was proved that if $f(\mathrm{a}/r)$ is positive the two spheres of liquid are too far apart to admit of junction, and if it is negative they are too near. Finally we found that all these solutions were unstable.

The solutions for the two spheres showed them to be always very close together, and as all the solutions for two ellipsoids, when they are in limiting stability, made them much further apart than were the two spheres, it seemed somewhat improbable that two ellipsoids could be similarly joined by a pipe, and certain that they would be unstable if such junction were possible. Nevertheless, it seemed conceivable that the additional terms, which must appear in $f(\mathrm{a}/r)$ when the constraint to spherical form is removed, might alter the conditions so that the junction of ellipsoids by a pipe should become possible. It thus became expedient to solve a problem analogous to that of § 3 when the two masses of liquid are ellipsoidal.

The conditions of equilibrium of two ellipsoids unjoined by a pipe are given in § 10, and the additional condition corresponding to junction by a pipe is

$$\frac{dV}{d\lambda} + \tfrac{1}{2}\omega^2 \frac{dI}{d\lambda} = 0.$$

In the present investigation I shall neglect the higher ellipticities, denoted f_i^s and F_i^s, and terms of higher order than those in $1/r^5$.

With this degree of approximation we have

$$V = (\tfrac{4}{3}\pi\rho\mathrm{a}^3)^2 \left[\frac{\lambda}{(1+\lambda)^2 r} + \tfrac{3}{10}\frac{\lambda^2}{(1+\lambda)^2}\psi + \tfrac{3}{10}\frac{1}{(1+\lambda)^2}\Psi\right] + (eE)_2,$$

where $(eE)_2$ is given in (14) (with omission of terms in $1/r^7$),

Also

$$\psi = \frac{2}{k}\int_{\nu_0}^{\infty} \frac{d\nu}{(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}},$$

and Ψ has a symmetrical form in $\mathcal{K}$ and K.

We have besides $\omega^2 = \tfrac{4}{3}\pi\rho \dfrac{\mathrm{a}^3}{r^3}(1+\zeta)$, where ζ is given in (24); and I is given in (22).

The differentiation with respect to λ and the subsequent re-arrangement of the equation are rather tedious, and I will not give the details of the operations. It may however be well to note that k, $\mathcal{K}$ are functions of λ, and that

$$\frac{d\psi}{d\lambda} = -\frac{1}{3\lambda(1+\lambda)}\psi, \quad \frac{d\Psi}{d\lambda} = \frac{1}{3(1+\lambda)}\Psi.$$

I find finally that the equation of condition is $f\left(\frac{\mathrm{a}}{r}\right) = 0$, where

$$\begin{aligned} f\left(\frac{\mathrm{a}}{r}\right) = & -\tfrac{9}{2}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}\frac{\mathrm{a}}{r} - \frac{3\mathrm{a}(\lambda\psi-\Psi)}{2(1+\lambda)^{1/3}(1-\lambda^{2/3})} \\ & - \frac{1}{(1+\lambda)^{1/3}(1-\lambda^{2/3})}\Bigg[\frac{\mathrm{a}c^2}{20r^3}\{48-20\lambda-(19-15\lambda)\cos^2\gamma-(9-25\lambda)\cos^2\beta\} \\ & \qquad + \frac{\mathrm{a}C^2}{20r^3}\{20-48\lambda-(15-19\lambda)\cos^2\Gamma-(25-9\lambda)\cos^2\mathrm{B}\} \\ & \qquad + \frac{3\mathrm{a}c^4}{560r^5}\{288-112\lambda-(260-140\lambda)\cos^2\gamma-(204-196\lambda)\cos^2\beta \\ & \qquad\qquad + (87-63\lambda)\cos^4\gamma+(59-91\lambda)\cos^4\beta \\ & \qquad\qquad\qquad + (30-70\lambda)\cos^2\beta\cos^2\gamma\} \\ & \qquad + \frac{3\mathrm{a}C^4}{560r^5}\{112-288\lambda-(140-260\lambda)\cos^2\Gamma-(196-204\lambda)\cos^2\mathrm{B} \\ & \qquad\qquad + (63-87\lambda)\cos^4\Gamma+(91-59\lambda)\cos^4\mathrm{B} \\ & \qquad\qquad\qquad + (70-30\lambda)\cos^2\mathrm{B}\cos^2\Gamma\} \\ & \qquad + \frac{3\mathrm{a}c^2C^2}{40r^5}\{40(1-\lambda)-(18-22\lambda)\cos^2\gamma-(22-18\lambda)\cos^2\Gamma \\ & \qquad\qquad -(14-26\lambda)\cos^2\beta-(26-14\lambda)\cos^2\mathrm{B} \\ & \qquad\qquad +15(1-\lambda)(\cos^2\gamma\cos^2\Gamma+\cos^2\beta\cos^2\mathrm{B}) \\ & \qquad\qquad +(7-3\lambda)\cos^2\gamma\cos^2\mathrm{B}+(3-7\lambda)\cos^2\Gamma\cos^2\beta\}\Bigg] \quad (44). \end{aligned}$$

In this expression c and C are respectively the longest semi-axes of the two ellipsoids, which are pointed at one another.

We may derive ψ and Ψ from LEGENDRE's tables of elliptic integrals for

$$\psi = \frac{2}{c\sin\gamma}F(\kappa,\gamma), \quad \Psi = \frac{2}{2C\sin\Gamma}F(\mathrm{K},\Gamma);$$

or we may expand the integrals in powers of $\kappa'^2\tan^2\gamma$ and obtain the approximate formula

$$\begin{aligned} \psi = \frac{2}{c}\big[1+(\Omega-1)(1+\tfrac{1}{4}\kappa'^2+\tfrac{9}{64}\kappa'^4+\tfrac{25}{256}\kappa'^6\ldots)-\tfrac{1}{4}\kappa'^2\tan^2\gamma(1+\tfrac{3}{16}\kappa'^2+\tfrac{25}{192}\kappa'^4\ldots) \\ +\tfrac{3}{32}\kappa'^4\tan^4\gamma(1+\tfrac{5}{36}\kappa'^2\ldots)-\tfrac{5}{96}\kappa'^6\tan^6\gamma(1+\ldots)\big] \quad . \quad (45), \end{aligned}$$

where $\Omega = \frac{1}{\sin\gamma}\log_e\frac{1+\sin\gamma}{\cos\gamma}$. The formula for Ψ is of course symmetrical.

It should be noted that when the two ellipsoids reduce to spheres, we have

$$\gamma=\beta=\Gamma=\mathrm{B}=0,\ c=\frac{\lambda^{1/3}\mathrm{a}}{(1+\lambda)^{1/3}},\ C=\frac{1}{(1+\lambda)^{1/3}}\mathrm{a},\ \psi=\frac{2}{c}=\frac{2}{\mathrm{a}}\frac{(1+\lambda)^{1/3}}{\lambda^{1/3}},\ \Psi=\frac{2}{\mathrm{a}}(1+\lambda)^{1/3}.$$

Thus

$$f\left(\frac{\mathrm{a}}{r}\right) = -\tfrac{9}{2}\frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})}\frac{\mathrm{a}}{r}+3+\frac{\mathrm{a}^3}{r^3}.$$

This is the form obtained in the solution of the restricted problem of § 3.

We conclude that if $f(\mathrm{a}/r)$, as expressed in (44), with values derived from any solution of the problem of the equilibrium of two ellipsoids unconnected by a pipe, is positive, the two figures are too far apart to admit of junction, and *vice versâ.* I have in fact always found it positive, although always diminishing as r diminishes, so that junction would seem to be always impossible, at least so long as the approximation retains any validity. This might indicate that there is no figure of equilibrium shaped like an hour-glass with a thin neck. However, I return to this subject in discussing numerical solutions, and in the summary of results.

In the case where the two masses are equal, $\lambda=1$, and the above formula for $f(\mathrm{a}/r)$ fails by becoming indeterminate. As this is a case of especial interest, it must be considered.

Since the two shapes are now exactly alike, we may take κ, γ, β, k to define either of them.

When $\lambda = 1$, the first term of $f(\mathrm{a}/r)$ becomes $-\dfrac{27}{4.2^{1/3}}\dfrac{\mathrm{a}}{r}$.

The second term becomes

$$-\frac{3\mathrm{a}\psi(\lambda-1)}{2(1+\lambda)^{1/3}(1-\lambda^{2/3})} = \frac{3\psi\mathrm{a}(1+\lambda^{1/3}+\lambda^{2/3})}{2(1+\lambda)^{1/3}(1+\lambda^{1/3})} = \frac{9\psi\mathrm{a}}{4.2^{1/3}}.$$

All the terms in $1/r^3$ are one of the two forms

$$F\left[\frac{c^2-\lambda C^2}{1-\lambda^{2/3}}\right] \quad \text{or} \quad G\left[\frac{\lambda c^2-C^2}{1-\lambda^{2/3}}\right].$$

Now,

$$c^2 = \frac{\mathrm{a}^2}{(\cos\beta\cos\gamma)^{2/3}}\frac{\lambda^{2/3}}{(1+\lambda)^{2/3}}, \quad C^2 = \frac{\mathrm{a}^2}{(\cos \mathrm{B}\cos \Gamma)^{2/3}}\frac{1}{(1+\lambda)^{2/3}}.$$

In the limit $\beta = \mathrm{B}$, $\gamma = \Gamma$, and $\lambda = 1$; and we find that the first of these forms becomes $\frac{1}{2}Fc^2$, and the second $-\frac{5}{2}Gc^2$.

Again, of the terms in $1/r^5$, those in c^4 and C^4 are of one of the two forms

$$F\left[\frac{c^4-\lambda C^4}{1-\lambda^{2/3}}\right] \quad \text{or} \quad G\left[\frac{\lambda c^4-C^4}{1-\lambda^{2/3}}\right].$$

In the limit the first of these reduces to $-\frac{1}{2}Fc^4$, and the second to $-\frac{7}{2}Gc^4$.

The last term in $1/r^7$ has a common factor $1-\lambda$, when $\gamma = \Gamma$, $\beta = \mathrm{B}$, and

$$\frac{1-\lambda}{(1+\lambda)^{1/3}(1-\lambda^{2/3})} = \frac{1+\lambda^{1/3}+\lambda^{2/3}}{(1+\lambda)^{1/3}(1+\lambda^{1/3})} = \frac{3}{2.2^{1/3}}.$$

By means of these transformations we find for $\lambda = 1$

$$f\left(\frac{\mathrm{a}}{r}\right) = \frac{3}{16^{1/3}}\Big[-\tfrac{9}{2}\frac{\mathrm{a}}{r} + \psi\mathrm{a} + \frac{\mathrm{a}c^2}{30r^3}(-74+47\cos^2\gamma+67\cos^2\beta)$$
$$+\frac{\mathrm{a}c^4}{70r^5}(-272+300\cos^2\gamma+356\cos^2\beta-123\cos^4\gamma-151\cos^4\beta$$
$$-110\cos^2\beta\cos^2\gamma)\Big]. \quad (46).$$

If we put $\beta = \gamma = 0$, and note that c becomes $\frac{\mathrm{a}}{2^{1/3}}$, this expression reduces as before to the correct form.

§ 14. *Ellipsoidal Harmonic Deformations of the Third Order.*

The two ellipsoids whose forms have been determined are subject to further deformation by harmonic inequalities. The expression for the ellipticity f_i^s corresponding to all the cosine-harmonic functions for i greater than 2 and s even is given in (25), viz. :—

$$f_i^s = -\tfrac{1}{3}(2i+1)\frac{\mathfrak{Q}_i^s(r/k)\,\mathfrak{P}_i^s(\nu_0)\,\mathfrak{P}_i^s(1)\,\mathfrak{C}_i^s(\tfrac{1}{2}\pi)}{\lambda\mathfrak{T}_i^s\left\{\mathfrak{A}_i^s-\mathsf{A}_1^1-\dfrac{k^3}{3\lambda r^3}\dfrac{\cos^2\gamma}{\sin^2\beta}\left[1+\dfrac{3(3+\kappa^2)}{14\kappa^2}\dfrac{k^2}{r^2}+\ldots\right]\right\}} \quad . \quad (47).$$

I shall begin by considering the ellipticities f_3 and f_3^2 corresponding to $i = 3$ and $s = 0, 2$.

I define

$$\mathfrak{P}_3^s(\nu) = \nu(\kappa^2\nu-q^2), \quad (s = 0, 2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48),$$

where $q^2 = \frac{2}{5}[1+\kappa^2\mp\surd(1-\frac{7}{4}\kappa^2+\kappa^4)]$, with upper sign for $s = 0$ and lower for $s = 2$.

Then

$$\mathfrak{Q}_3^s(\nu) = \mathfrak{P}_3^s(\nu)\int_\nu^\infty \frac{d\nu}{[\mathfrak{P}_3^s(\nu)]^2(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}}.$$

Since ν is always greater than unity, the function under the integral sign may be expanded in powers of $1/\nu$, as in (7), (8), (9) of § 5, and the integration may then be effected. In this way I find

$$\mathfrak{Q}_3^s(\nu) = \frac{1}{7\kappa^2\nu^4}\left\{1+\frac{7(1+\kappa^2)+10q^2}{2.9\kappa^2\nu^2}+\frac{7[9(3\kappa^4+2\kappa^2+3)+28q^2(\kappa^2+1)+40q^4]}{8.9.11\kappa^4\nu^4}+\ldots\right\} \quad (49).$$

In all the cases we have to consider κ^2 is nearly unity and κ'^2 is small. Then, since $q^2 = \frac{1}{5}[4-2\kappa'^2\mp\surd(1-\kappa'^2+4\kappa'^4)]$, and since the function under the square root may be expanded in powers of κ'^2, we may obtain approximate expressions for q^2 in the two cases $s = 0$, $s = 2$.

When $s = 0$, we have

$$q^2 = \tfrac{3}{5}(1-\tfrac{1}{2}\kappa'^2-\tfrac{5}{8}\kappa'^4-\tfrac{5}{16}\kappa'^6\ldots).$$

When $s = 2$,

$$q^2 = 1-\tfrac{1}{2}\kappa'^2+\tfrac{3}{8}\kappa'^4+\tfrac{3}{16}\kappa'^6\ldots$$

If we substitute these values for q^2 in (49), and express the functions of κ^2 therein in terms of κ'^2, we obtain the following results:—

$$\mathfrak{Q}_3\left(\frac{k}{r}\right) = \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{10}{9}\left(1+\tfrac{1}{2}\kappa'^2+\tfrac{5}{16}\kappa'^4+\tfrac{7}{32}\kappa'^6\ldots\right)\frac{k^2}{r^2}+\tfrac{35}{33}\left(1+\kappa'^2+\kappa'^4+\kappa'^6\ldots\right)\frac{k^4}{r^4}\ldots\right\}$$

$$\mathfrak{Q}_3^{\,2}\left(\frac{k}{r}\right) = \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{4}{3}\left(1+\tfrac{1}{2}\kappa'^2+\tfrac{21}{32}\kappa'^4+\tfrac{47}{64}\kappa'^6\ldots\right)\frac{k^2}{r^2}+\tfrac{49}{33}\left(1+\kappa'^2+\tfrac{45}{28}\kappa'^4+\tfrac{31}{14}\kappa'^6\ldots\right)\frac{k^4}{r^4}\ldots\right\}.$$

Shorter forms may be given to these by making the expansions run in powers of $1/\kappa r^2$; we then have

$$\left.\begin{aligned}\mathfrak{Q}_3\left(\frac{k}{r}\right) &= \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{10}{9}\left(1+0\kappa'^2-\tfrac{1}{16}\kappa'^4-\tfrac{1}{8}\kappa'^6\ldots\right)\frac{k^2}{\kappa r^2}+\tfrac{35}{33}\frac{k^4}{\kappa^2 r^4}\ldots\right\}\\ \mathfrak{Q}_3^{\,2}\left(\frac{k}{r}\right) &= \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{4}{3}\left(1+0\kappa'^2+\tfrac{9}{32}\kappa'^4+\tfrac{9}{32}\kappa'^6\ldots\right)\frac{k^2}{\kappa r^2}+\tfrac{49}{33}\left(1+0\kappa'^2+\tfrac{17}{28}\kappa'^4+\tfrac{17}{28}\kappa'^6\ldots\right)\frac{k^4}{\kappa^2 r^4}\ldots\right\}\end{aligned}\right\} \quad (50).$$

It will however suffice for our purposes to take

$$\left.\begin{aligned}\mathfrak{Q}_3\left(\frac{k}{r}\right) &= \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{10}{9}\frac{k^2}{\kappa r^2}\right\}\\ \mathfrak{Q}_3^{\,2}\left(\frac{k}{r}\right) &= \frac{k^4}{7\kappa^2 r^4}\left\{1+\tfrac{4}{3}\frac{k^2}{\kappa r^2}\right\}\end{aligned}\right\} \quad \ldots\ldots\ldots \quad (51).$$

The next task is to determine the product $\mathfrak{P}_3^{\,s}(\nu_0)\,\mathfrak{P}_3^{\,s}(1)\,\mathsf{C}_3^{\,s}(\tfrac{1}{2}\pi)$ $(s = 0,\ 2)$.

The form of the ellipsoid is determined by ν_0, where $\nu_0 = \dfrac{1}{\kappa\sin\gamma} = \dfrac{1}{\sin\beta}$.

If we write $\Delta_1^{\,2} = 1-q^2\sin^2\gamma$, with the definition of $\mathfrak{P}_3^{\,s}$ given above in (48), we have

$$\mathfrak{P}_3^{\,s}(\nu_0) = \frac{\Delta_1^{\,2}}{\kappa\sin^3\gamma} \quad \ldots\ldots\ldots \quad (52).$$

It will be remembered that q has a different value according as $s = 0$ or 2.

I now make the following definitions,

$$\mathfrak{P}_3^{\,s}(\mu) = \mu\left(\kappa^2\mu^2-q^2\right), \quad \mathsf{C}_3^{\,s}(\phi) = \left(q'^2-\kappa'^2\cos^2\phi\right)\surd\left(1-\kappa'^2\cos^2\phi\right);$$

so that

$$\mathfrak{P}_3^{\,s}(1)\,\mathsf{C}_3^{\,s}(\tfrac{1}{2}\pi) = q'^2\left(\kappa^2-q^2\right) \quad \ldots\ldots\ldots \quad (53).$$

It is easy to show that rigorously

$$q'^2\left(\kappa^2-q^2\right) = \tfrac{2}{25}\left[1-\kappa'^2-\kappa'^4\pm\left(1-\tfrac{1}{2}\kappa'^2\right)\surd\left(1-\kappa'^2+4\kappa'^4\right)\right] \quad (s = 0,\ 2).$$

Whence approximately, with the upper sign for $s = 0$,

$$q'^2\left(\kappa^2-q^2\right) = \tfrac{4}{25}\left(1-\kappa'^2+\tfrac{9}{16}\kappa'^4+0\kappa'^6\ldots\right) \quad \ldots\ldots\ldots \quad (54).$$

With the lower sign for $s = 2$,

$$q'^2(\kappa^2 - q^2) = -\tfrac{1}{4}\kappa'^4(1 + 0\kappa'^2 - \tfrac{9}{16}\kappa'^4 \ldots) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55).$$

The three last expressions (53), (54), (55), give the two values of $\mathfrak{P}_3^s(1)\,\mathsf{C}_3^s(\tfrac{1}{2}\pi)$.

We now turn to the functions $\mathfrak{T}_3^s$. The general definition of § 5 was

$$\mathfrak{T}_i^s = \frac{(2i+1)\rho}{3M}\int[\mathfrak{P}_i^s(\mu)\,\mathfrak{C}_i^s(\phi)]^2 p\,d\sigma,$$

where M was the mass of the ellipsoid. Hence in the cases under consideration

$$\mathfrak{T}_3^s = \frac{7\sin^3\beta}{4\pi k^3\cos\beta\cos\gamma}\int[\mathfrak{P}_3^s(\mu)\,\mathsf{C}_3^s(\phi)]^2 p\,d\sigma \quad (s = 0, 2).$$

These integrals are evaluated in (38) of my paper on 'Integrals'; whence I find

$$\mathfrak{T}_3^s = \frac{2^3}{5^4}D[(1-\tfrac{1}{2}\kappa'^2)(1-\kappa'^2-\tfrac{8}{3}\kappa'^4)+(1-\kappa'^2+\tfrac{2}{3}\kappa'^4)D],$$

where $D = \pm\sqrt{(1-\kappa'^2+4\kappa'^4)}$, with upper sign for $s = 0$ and lower for $s = 2$.

It will, however, suffice if we use the development of D in powers of κ'^2. The result is, in fact, given in the equations next below (38) in 'Integrals,' and they are

$$\left.\begin{aligned} \mathfrak{T}_3 &= (\tfrac{2}{5})^4(1-2\kappa'^2+\tfrac{49}{16}\kappa'^4\ldots), \\ \mathfrak{T}_3^2 &= \tfrac{1}{3.5}\kappa'^4(1-\kappa'^2+\tfrac{31}{16}\kappa'^4\ldots). \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56).$$

From (53), (54), (55), and (56) we now find

$$\left.\begin{aligned} \frac{\mathfrak{P}_3(1)\,\mathsf{C}_3(\tfrac{1}{2}\pi)}{\mathfrak{T}_3} &= \tfrac{25}{4}\,\frac{1-\kappa'^2+\tfrac{9}{16}\kappa'^4\ldots}{1-2\kappa'^2+\tfrac{49}{16}\kappa'^4\ldots} = \tfrac{25}{4}(1+\kappa'^2-\tfrac{1}{2}\kappa'^4\ldots), \\ \frac{\mathfrak{P}_3^2(1)\,\mathsf{C}_3^2(\tfrac{1}{2}\pi)}{\mathfrak{T}_3^2} &= -\tfrac{15}{4}\,\frac{1+0\kappa'^2-\tfrac{9}{16}\kappa'^4\ldots}{1-\kappa'^2+\tfrac{31}{16}\kappa'^4\ldots} = -\tfrac{15}{4}(1+\kappa'^2-\tfrac{3}{2}\kappa'^4\ldots). \end{aligned}\right\} \quad . \quad (57).$$

Thus from (51), (52), (57), we find

$$\left.\begin{aligned} -\frac{7}{3\lambda\mathfrak{T}_3}\mathfrak{Q}_3\left(\frac{r}{k}\right)\mathfrak{P}_3(\nu_0)\,\mathfrak{P}_3(1)\,\mathsf{C}_3(\tfrac{1}{2}\pi) &= -\frac{25\Delta_1^2}{12\lambda\sin^3\beta}(1+\kappa'^2-\tfrac{1}{2}\kappa'^4\ldots)\frac{k^4}{r^4}\left(1+\tfrac{10}{9}\frac{k^2}{\kappa r^2}\right), \\ -\frac{7}{3\lambda\mathfrak{T}_3^2}\mathfrak{Q}_3^2\left(\frac{r}{k}\right)\mathfrak{P}_3^2(\nu_0)\,\mathfrak{P}_3^2(1)\,\mathsf{C}_3^2(\tfrac{1}{2}\pi) &= \frac{5\Delta_1^2}{4\lambda\sin^3\beta}(1+\kappa'^2-\tfrac{3}{2}\kappa'^4)\frac{k^4}{r^4}\left(1+\tfrac{4}{3}\frac{k^2}{\kappa r^2}\right). \end{aligned}\right\} (58).$$

By (47) f_3^s is equal to the above expressions divided by

$$\mathfrak{A}_3^s - \mathbf{A}_1^1 - \frac{k^3}{3\lambda r^3}\frac{\cos^2\gamma}{\sin^2\beta}\left[1+\frac{3(3+\kappa^2)}{14\kappa^2}\frac{k^2}{r^2}\ldots\right].$$

It therefore remains to determine $\mathfrak{A}_3^s$ and $\mathbf{A}_1^1$.

In order to find $\mathsf{A}_1^{\,1}$ we expand Δ in powers of $\kappa'^2 \tan^2 \gamma$. Thus

$$\mathsf{A}_1^{\,1} = \kappa \cot^2 \gamma \int_0^\gamma \frac{\tan^2 \gamma}{\Delta}\, d\gamma = \kappa \cot^2 \gamma \int_0^\gamma \frac{\sin^2 \gamma}{\cos^3 \gamma} \left(1 - \tfrac{1}{2}\kappa'^2 \tan^2 \gamma + \tfrac{3}{8}\kappa'^4 \tan^4 \gamma \ldots\right) d\gamma\,;$$

whence

$$\mathsf{A}_1^{\,1} = \frac{\kappa}{2 \sin \gamma} \left\{\left[1 + \tfrac{3}{8}\kappa'^2 + \tfrac{15}{64}\kappa'^4\right]\left[1 - \cos^2 \gamma\, \Omega\right] - \tfrac{1}{4}\kappa'^2 \tan^2 \gamma \left(1 + \tfrac{5}{8}\kappa'^2\right) + \tfrac{1}{8}\kappa'^4 \tan^4 \gamma\right\}.$$

The result may, of course, be obtained with higher accuracy if it be desired to do so. By (25) of the 'Pear-shaped Figure'

$$\mathfrak{A}_3^{\,s} = \mathfrak{P}_3^{\,s}(\nu_0)\, \mathfrak{Q}_3^{\,s}(\nu_0) = \frac{\kappa \Delta_1^{\,4}}{\sin^6 \gamma} \int_0^\gamma \frac{\sin^6 \gamma}{\Delta_1^{\,4}\, \Delta}\, d\gamma,$$

where $\Delta_1^{\,2} = 1 - q^2 \sin^2 \gamma$, with appropriate values of q for $s = 0$ and 2 respectively.

It is clear that under the integral sign $1/\Delta$ may be expanded in powers of $\kappa'^2 \tan^2 \gamma$, but this is not possible with $1/\Delta_1^{\,4}$.

The two cases $s = 0, 2$ have to be treated by different methods, and I begin with $\mathfrak{A}_3$, where $s = 0$.

Since

$$\frac{1}{\Delta} = \frac{1}{\cos \gamma}\left[1 + \tfrac{1}{2}\kappa'^2 \tan^2 \gamma + \tfrac{3}{8}\kappa'^4 \tan^4 \gamma \ldots\right],$$

it is necessary to consider the integrals with respect to γ of the functions

$$\frac{\sin^6 \gamma}{\cos \gamma\, \Delta_1^{\,4}}, \quad \frac{\sin^8 \gamma}{\cos^3 \gamma\, \Delta_1^{\,4}}, \quad \frac{\sin^{10} \gamma}{\cos^5 \gamma\, \Delta_1^{\,4}}.$$

Writing $x = \sin \gamma$, and $q^2 = \dfrac{1}{a^2}$, this is seen to be equivalent to finding

$$\int \frac{x^6\, dx}{(1-x^2)(a^2-x^2)^2}, \quad \int \frac{x^8\, dx}{(1-x^2)^2 (a^2-x^2)^2}, \quad \int \frac{x^{10}\, dx}{(1-x^2)^3 (a^2-x^2)^2}.$$

Now

$$\frac{x^6}{(1-x^2)(a^2-x^2)^2} = -1 + \frac{1}{2(a^2-1)^2}\left(\frac{1}{1-x} + \frac{1}{1+x}\right) - \frac{a^4}{4(a^2-1)}\left(\frac{1}{(a-x)^2} + \frac{1}{(a+x)^2}\right)$$
$$+ \frac{a^3(3a^2-5)}{4(a^2-1)^2}\left(\frac{1}{a-x} + \frac{1}{a+x}\right),$$

$$\frac{x^8}{(1-x^2)^2(a^2-x^2)^2} = 1 - \frac{7a^2-3}{4(a^2-1)^3}\left(\frac{1}{1-x} + \frac{1}{1+x}\right) + \frac{1}{4(a^2-1)^2}\left(\frac{1}{(1-x)^2} + \frac{1}{(1+x)^2}\right)$$
$$- \frac{a^5(3a^2-7)}{4(a^2-1)^3}\left(\frac{1}{a-x} + \frac{1}{a+x}\right) + \frac{a^6}{4(a^2-1)^2}\left(\frac{1}{(a-x)^2} + \frac{1}{(a+x)^2}\right),$$

$$\frac{x^{10}}{(1-x^2)^3(a^2-x^2)^2} = -1 + \frac{3(21a^4-18a^2+5)}{16(a^2-1)^4}\left(\frac{1}{1-x} + \frac{1}{1+x}\right) - \frac{17a^2-9}{16(a^2-1)^3}\left(\frac{1}{(1-x)^2} + \frac{1}{(1+x)^2}\right)$$
$$+ \frac{1}{8(a^2-1)^2}\left(\frac{1}{(1-x)^3} + \frac{1}{(1+x)^3}\right) + \frac{3a^7(a^2-3)}{4(a^2-1)^4}\left(\frac{1}{a-x} + \frac{1}{a+x}\right)$$
$$- \frac{a^8}{4(a^2-1)^3}\left(\frac{1}{(a-x)^2} + \frac{1}{(a+x)^2}\right).$$

Each term in these expressions is integrable, and the limits of integration are $x = \sin\gamma$ to 0. After integration a must be put equal to $1/q$, and since the result will only be true as far as κ'^4 we must put for q^2 its approximate value $\frac{3}{5}(1-\frac{1}{2}\kappa'^2-\frac{5}{8}\kappa'^4)$.

When these processes are carried out, and the formulæ combined, we find

$$\mathfrak{A}_3 = \frac{\Delta_1^{\,4}}{q^4\sin^5\gamma}\Big\{-1+\tfrac{9}{4}(1+\tfrac{1}{4}\kappa'^2+\tfrac{23}{64}\kappa'^4)\,\Omega-\tfrac{5}{4}(1+0\kappa'^2-\tfrac{9}{32}\kappa'^4)\frac{1}{\Delta_1^{\,2}}$$
$$-\tfrac{9}{16}\kappa'^2\sec^2\gamma\,(1+\tfrac{39}{16}\kappa'^2)+\tfrac{27}{128}\kappa'^4\sec^4\gamma\Big\} \quad . \quad . \quad . \quad (59).$$

In the coefficient and in $\Delta_1^{\,2}$ (or $1-q^2\sin^2\gamma$) it is as easy to use the rigorous value of q^2 as the approximate one, so it may be well to repeat that

$$q^2 = \tfrac{2}{5}\left[1+\kappa^2-\sqrt{(1-\tfrac{7}{4}\kappa^2+\kappa^4)}\right], \text{ and } \Omega = \frac{1}{\sin\gamma}\log_e\frac{1+\sin\gamma}{\cos\gamma}.$$

If a process parallel to that adopted for finding $\mathfrak{A}_3$ were adopted in the case of $\mathfrak{A}_3^{\,2}$, it would lead to a divergent series, but fortunately a much simpler process is available.

In the case of $i = 3$, $s = 2$, we have $q^2 = 1-\frac{1}{2}\kappa'^2+\frac{3}{8}\kappa'^4\ldots$, so that

$$\Delta_1^{\,2} = \cos^2\gamma\,[1+\tfrac{1}{2}\kappa'^2(1-\tfrac{3}{4}\kappa'^2)\tan^2\gamma].$$

Accordingly we are now able to expand $1/\Delta_1^{\,4}$ in powers of $\kappa'^2\tan^2\gamma$.

We have then

$$\frac{1}{\Delta_1^{\,4}} = \frac{1}{\cos^4\gamma}\,[1-\kappa'^2(1-\tfrac{3}{4}\kappa'^2)\tan^2\gamma+\tfrac{3}{4}\kappa'^4\tan^4\gamma\ldots],$$

$$\frac{1}{\Delta} = \frac{1}{\cos\gamma}\,[1-\tfrac{1}{2}\kappa'^2\tan^2\gamma+\tfrac{3}{8}\kappa'^4\tan^4\gamma\ldots].$$

Whence

$$\frac{\sin^6\gamma}{\Delta\Delta_1^{\,4}} = \frac{\sin^6\gamma}{\cos^5\gamma}\,[1-\tfrac{3}{2}\kappa'^2(1-\tfrac{1}{2}\kappa'^2)\tan^2\gamma+\tfrac{13}{8}\kappa'^4\tan^4\gamma\ldots].$$

Now

$$\int_0^\gamma\frac{\sin^6\gamma}{\cos^5\gamma}\,d\gamma = \sin\gamma\,[\tfrac{1}{4}\tan^4\gamma-\tfrac{5}{4\cdot2}\tan^2\gamma+\tfrac{5\cdot3}{4\cdot2}(\Omega-1)],$$

$$\int_0^\gamma\frac{\sin^8\gamma}{\cos^7\gamma}\,d\gamma = \sin\gamma\,[\tfrac{1}{6}\tan^6\gamma-\tfrac{7}{6\cdot4}\tan^4\gamma+\tfrac{7\cdot5}{6\cdot4\cdot2}\tan^2\gamma-\tfrac{7\cdot5\cdot3}{6\cdot4\cdot2}(\Omega-1)],$$

$$\int_0^\gamma\frac{\sin^{10}\gamma}{\cos^9\gamma}\,d\gamma = \sin\gamma\,[\tfrac{1}{8}\tan^8\gamma-\tfrac{9}{8\cdot6}\tan^6\gamma+\tfrac{9\cdot7}{8\cdot6\cdot4}\tan^4\gamma-\tfrac{9\cdot7\cdot5}{8\cdot6\cdot4\cdot2}\tan^2\gamma+\tfrac{9\cdot7\cdot5\cdot3}{8\cdot6\cdot4\cdot2}(\Omega-1)],$$

where

$$\Omega = \frac{1}{\sin\gamma}\log_e\frac{1+\sin\gamma}{\cos\gamma}.$$

Combining these formulæ, I find

$$\mathfrak{A}_3^{\,2} = \frac{\Delta_1^{\,4}}{4\sin^5\gamma}\left[\{\tan^4\gamma - \tfrac{5}{2}\tan^2\gamma + \tfrac{15}{2}(\Omega-1)\}\{1+\tfrac{5}{4}\kappa'^2 + \tfrac{33}{128}\kappa'^4\}\right.$$
$$\left. -\kappa'^2(1+\tfrac{7}{32}\kappa'^2)\tan^6\gamma + \tfrac{13}{16}\kappa'^4\tan^8\gamma\right] \quad . \quad . \quad (60).$$

The form is somewhat awkward, but I have not been able to reduce it to any better shape.

§ 15. *The Values of $\mathfrak{Q}_i^s$ for Higher Harmonic Terms.*

For higher harmonic terms it is necessary to adopt the approximate forms of the functions investigated in "Harmonics." The development is there carried out in powers of a parameter β, which I will now write β_0 to avoid confusion; this parameter is equal to $\dfrac{1-\kappa^2}{1+\kappa^2}$, or to $\tfrac{1}{2}\kappa'^2 + \tfrac{1}{4}\kappa'^4 \ldots$ of the present paper.

The functions are here defined by

$$\mathfrak{Q}_i^s(\nu) = \mathfrak{P}_i^s(\nu)\int_\nu^\infty \frac{d\nu}{[\mathfrak{P}_i^s(\nu)]^2(\nu^2-1)^{1/2}\left(\nu^2 - \dfrac{1+\beta_0}{1-\beta_0}\right)^{1/2}};$$

but in the notation of § 10 of "Harmonics" this would be called $\mathfrak{Q}_i^s(\nu)/\mathfrak{E}_i^s$. Thus, if $[\mathfrak{Q}_i^s(\nu)]$ denotes that function as defined in "Harmonics," we have

$$\mathfrak{Q}_i^s(\nu) = \frac{[\mathfrak{Q}_i^s(\nu)]}{\mathfrak{E}_i^s}.$$

We have for the approximate expression for $\mathfrak{P}_i^s$

$$\mathfrak{P}_i^s(\nu) = P_i^s(\nu) + \beta_0 q_{s-2} P_i^{s-2}(\nu) + \beta_0 q_{s+2} P_i^{s+2}(\nu) + \beta_0^{\,2} q_{s-4} P_i^{s-4}(\nu) + \beta_0^{\,2} q_{s+4} P_i^{s+4}(\nu).$$

The investigation on p. 500 of "Harmonics" shows that the leading term of $[\mathfrak{Q}_i^s(\nu)]$ is

$$(-)^s \frac{2^i\, i\,!}{2i+1\,!}\,\frac{i+s\,!}{\nu^{i+1}}\left[1 + \beta_0 q_{s-2}\frac{i+s-2\,!}{i+s\,!} + \beta_0 q_{s+2}\frac{i+s+2\,!}{i+s\,!}\right.$$
$$\left. + \beta_0^{\,2} q_{s-4}\frac{i+s-4\,!}{i+s\,!} + \beta_0^{\,2} q_{s+4}\frac{i+s+4\,!}{i+s\,!}\right].$$

This has to be divided by $\mathfrak{E}_i^s$, the formula for which is given in § 10 of "Harmonics," and we thus obtain the leading term of $\mathfrak{Q}_i^s(\nu)$.

For the second term it will suffice if we take β_0 as zero, so that it is only necessary to consider $Q_i^s(\nu)$, which is equal to $(\nu^2-1)^{s/2}\dfrac{d^s}{d\nu^s}Q_i(\nu)$.

Since

$$Q_i(\nu) = \frac{2^i\,(i\,!)^2}{2i+1\,!}\left[\frac{1}{\nu^{i+1}} + \frac{i+2\,!}{2.1\,!\,i\,!}\,\frac{1}{(2i+3)\nu^{i+3}} + \ldots\right],$$

by differentiation, and by expansion of $(\nu^2-1)^{s/2}$ in powers of $1/\nu^2$ we obtain

$$Q_i^s(\nu) = (-)^s\,\frac{2^i.i\,!\,.\,i+s\,!}{2i+1\,!\;\nu^{i+1}}\left[1+\frac{(i+2)\,(i+1)+s^2}{2\,(2i+3)\,\nu^2} + \ldots\right].$$

Accordingly, in order to find the second term to the degree of approximation adopted, it is merely necessary to multiply the leading term by

$$1 + \frac{(i+2)\,(i+1)+s^2}{2\,(2i+3)\,\nu^2}.$$

In order to find the leading term explicitly we have to insert for the q's their values, and after some tedious reductions I find

$$\mathfrak{Q}_i^s\left(\frac{r}{k}\right) = \frac{2^i.i\,!\;i-s\,!}{2i+1\,!}\,\frac{k^{i+1}}{r^{i+1}}\left\{1+\tfrac{1}{4}\beta_0\,(\Sigma+2i)+\tfrac{1}{64}\beta_0{}^2\left[-2\Upsilon+\Sigma^2\,(s^2+3)\right.\right.$$
$$\left.\left.+2\Sigma\,(6i-1+2s^2)+2i\,(3i+1)-s^2\right]\right\} \times \left\{1+\frac{(i+2)\,(i+1)+s^2}{2\,(2i+3)}\,\frac{k^2}{r^2}\right\} \quad . \quad . \quad (61),$$

where

$$\Sigma = \frac{i\,(i+1)}{s^2-1}, \quad \Upsilon = \frac{(i-1)\,i\,(i+1)\,(i+2)}{s^2-4}.$$

This formula fails for the cases of $s = 0$ and $s = 2$, and these cases have to be treated apart. Following a parallel procedure I find

$$\mathfrak{Q}_i^2\left(\frac{r}{k}\right) = \frac{2^i.i\,!\,i-2\,!}{2i+1\,!}\,\frac{k^{i+1}}{r^{i+1}}\left\{1+\tfrac{1}{4}\beta_0\,(\Sigma+2i)+\tfrac{1}{512}\beta_0{}^2\left[29\Sigma^2+(144i+298)\,\Sigma-48i-40\right]\right\}$$
$$\times\left\{1+\frac{(i+2)\,(i+1)+4}{2\,(2i+3)}\,\frac{k^2}{r^2}\right\} . \quad (62).$$

$$\mathfrak{Q}_i\left(\frac{r}{k}\right)=\frac{2^i\,(i\,!)^2}{2i+1\,!}\,\frac{k^{i+1}}{r^{i+1}}\left\{1-\tfrac{1}{4}\beta_0 i(i-1)+\tfrac{1}{128}\beta_0{}^2 i(i-1)(7i^2-3i-6)\right\}\left\{1+\frac{(i+2)(i+1)}{2(2i+3)}\,\frac{k^2}{r^2}\right\}(63).$$

The values for i less than 3 are not required, and when $i = 3$ these formulæ are found to agree *mutatis mutandis* with those of the last section.

It is pretty clear from general considerations that the higher inequalities corresponding to harmonics other than the zonal ones must be very small. I have, in fact, computed the third tesseral harmonic inequality ($i = 3$, $s = 2$), and find that it is so very minute compared with the third zonal inequality ($i = 3$, $s = 0$) as to be negligible. Accordingly it appeared to be a waste of time to develop formulæ for any other than zonal inequalities for values of i greater than 3. Thus of the formulæ just determined the only one of which actual use is made is (63).

§ 16. *The Fourth Zonal Harmonic Inequality.*

In developing the expressions for the higher harmonic inequalities it seems to be most convenient to retain the parameter β_0, which is equal to $\frac{1-\kappa^2}{1+\kappa^2}$, instead of developing in powers of κ'^2 as heretofore.

On putting $i = 4$ in (63), we find

$$\mathfrak{Q}_4\left(\frac{r}{k}\right) = \frac{8}{5\cdot7\cdot9}\frac{k^5}{r^5}\left(1+\tfrac{15}{11}\frac{k^2}{r^2}\right)(1-3\beta_0+\tfrac{141}{16}\beta_0^2).$$

With the notation of "Harmonics" we have

$$\mathfrak{P}_4(\nu) = P_4(\nu)+\tfrac{1}{4}\beta_0 P_4^2(\nu)+\tfrac{1}{128}\beta_0^2 P_4^4(\nu),$$

$$\mathfrak{C}_4(\phi) = 1-5\beta_0\cos 2\phi+\tfrac{35}{16}\beta_0^2\cos 4\phi.$$

Accordingly

$$\mathfrak{P}_4(1) = P_4(1) = 1,$$

$$\mathfrak{C}_4(\tfrac{1}{2}\pi) = 1+5\beta_0+\tfrac{35}{16}\beta_0^2.$$

Again, from § 22 of "Harmonics" for type EEC, $i = 4$, $s = 0$, we have

$$\int[\mathfrak{P}_4\mathfrak{C}_4]^2 p\,d\sigma = \tfrac{4}{9}\pi k^3\nu_0(\nu_0^2-1)^{1/2}\left(\nu_0^2-\frac{1+\beta_0}{1-\beta_0}\right)^{1/2}[1+10\beta_0+\tfrac{325}{8}\beta_0^2].$$

But $\mathfrak{T}_4$ is this integral multiplied by 9 and divided by 3 times the volume of the ellipsoid.

Therefore

$$\mathfrak{T}_4 = 1+10\beta_0+\tfrac{325}{8}\beta_0^2.$$

In this formula the coefficients of the powers of β_0 increase with great rapidity, and the approximation may not be very satisfactory; nevertheless it is the best attainable without an enormous increase of labour.

Combining our several results

$$-\frac{9}{3\lambda\mathfrak{T}_4}\mathfrak{Q}_4\left(\frac{r}{k}\right)\mathfrak{P}_4(1)\,\mathfrak{C}_4(\tfrac{1}{2}\pi) = -\frac{8}{105\lambda}\frac{k^5}{r^5}\left(1+\tfrac{15}{11}\frac{k^2}{r^2}\right)(1-8\beta_0+\tfrac{283}{8}\beta_0^2) \quad . \quad (64).$$

It remains to find $\mathfrak{P}_4(\nu_0)$, and the denominator in the expression for f_4 which involves $\mathfrak{A}_4-\mathsf{A}_1^1$.

We have

$$\mathfrak{A}_4 = \mathfrak{P}_4(\nu_0)\,\mathfrak{Q}_4(\nu_0)$$

$$= [\mathfrak{P}_4(\nu_0)]^2\int_{\nu_0}^{\infty}\frac{d\nu}{[\mathfrak{P}_4(\nu)]^2(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}}.$$

Inside the integral sign I write $\nu = \frac{1}{\kappa\sin\psi}$ and change the independent variable to ψ; I also put $\sin\chi = \kappa \sin\psi$. At the surface of the ellipsoid we have $\psi = \gamma$, $\chi = \beta$, and since $\nu_0 = \dfrac{1}{\kappa\sin\gamma} = \dfrac{1}{\sin\beta}$, these are the values to be used in $\mathfrak{P}_4(\nu_0)$ outside the integral sign.

Then we have

$$\int_{\nu_0}^{\infty} \frac{d\nu}{(\nu^2-1)^{1/2}(\nu^2-1/\kappa^2)^{1/2}} = \kappa\int_0^{\gamma} \sec\chi \, d\psi.$$

Since

$$\begin{aligned} P_4(\nu) &= \tfrac{35}{8}(\nu^2-1)^4+5(\nu^2-1)+1 &&= 1+5\cot^2\chi+\tfrac{35}{8}\cot^4\chi, \\ P_4^2(\nu) &= \tfrac{15}{2}(\nu^2-1)[7(\nu^2-1)+6] &&= \tfrac{15}{2}(6\cot^2\chi+7\cot^4\chi), \\ P_4^4(\nu) &= 105(\nu^2-1)^2 &&= 105\cot^4\chi. \end{aligned}$$

Since further

$$\mathfrak{P}_4(\nu) = P_4(\nu)+\tfrac{1}{4}\beta_0 P_4^2(\nu)+\tfrac{1}{128}\beta_0^2 P_4^4(\nu),$$

we find

$$\left.\begin{aligned} \mathfrak{P}_4(\nu) &= 1+a\cot^2\chi+b\cot^4\chi, \\ a &= 5(1+\tfrac{9}{4}\beta_0), \\ b &= \tfrac{35}{8}(1+3\beta_0+\tfrac{3}{16}\beta_0^2). \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (65)$$

where

It must be noted further that when $\nu = \nu_0$ at the surface of the ellipsoid, $\chi = \beta$.

It follows then that $\mathfrak{P}_4(\nu_0) = 1+a\cot^2\beta+b\cot^4\beta$; and from (64)

$$-\frac{9}{3\lambda\mathfrak{T}_4}\mathfrak{Q}_4\left(\frac{r}{k}\right)\mathfrak{P}_4(\nu_0)\,\mathfrak{P}_4(1)\,\mathfrak{C}_4(\tfrac{1}{2}\pi) = -\frac{8}{105\lambda}\frac{k^5}{r^5}\left(1+\tfrac{15}{11}\frac{k^2}{r^2}\right)$$
$$(1-8\beta_0+\tfrac{283}{8}\beta_0^2)(1+a\cot^2\beta+b\cot^4\beta).$$

It remains to consider the evaluation of $\mathfrak{A}_4$, which now assumes the form

$$\mathfrak{A}_4 = \kappa\int_0^{\gamma}\left(\frac{1+a\cot^2\beta+b\cot^2\beta}{1+a\cot^2\chi+b\cot^2\chi}\right)^2 \sec\chi\, d\psi.$$

It would no doubt be possible to split the subject of integration into partial fractions, and thus obtain an accurate value as was done in the case of $\mathfrak{A}_3$, but it does not seem worth while to undertake so heavy a task, because a sufficiently exact value may be obtained by quadratures.

The method is employed in § 18, p. 294, in my paper on "Stability," and may be explained very shortly.

I divide γ into 10 or 12 equal parts—say 10 for brevity—and let $\delta = \frac{1}{10}\gamma$.

I then compute eleven equidistant values of the subject of integration, say u_0, u_1, … u_{10}, corresponding to $\psi = 0, 2\delta, 3\delta, \ldots 10\delta$. As a fact it is unnecessary to compute the first four of these, because they are practically zero.

The equidistant values increase so rapidly that they are very inappropriate for the application of the rules of numerical quadratures. Accordingly I take an empirical and integrable function, say v, such that $v_{12} = u_{12}$ and $v_{11} = u_{11}$, and apply the rules of quadrature only to the differences $u_n - v_n$. The result is a correction to the integral $\int_0^\gamma v\, d\psi$.

The empirical function which satisfies these conditions is

$$v = u_{10} e^{\frac{\psi-\gamma}{\delta} \log_e \frac{u_{10}}{u_9}}.$$

When $\psi = \gamma = 10\delta$, $v = u_{10}$; and when $\psi = 9\delta$, $v = u_{10} e^{-\log_e \frac{u_{10}}{u_9}} = u_9$.

Then $\int_0^\gamma v\, d\psi = \frac{u_{10}\delta}{\log_e (u_{10}/u_9)} (1 - e^{-10 \log_e (u_{10}/u_9)})$.

In the cases we have to treat $e^{-10 \log_e (u_{10}/u_9)}$ is an extremely small fraction, so that practically $\int_0^\gamma v\, d\psi = \frac{u_{10}\gamma}{10 \log_e (u_{10}/u_9)}$; and this is the function to be corrected by the result of quadrature.

For the quadratures we have

$$v_{10} = u_{10}, \quad v_9 = u_9, \quad v_8 = u_{10}\left(\frac{u_9}{u_{10}}\right)^2, \quad v_7 = u_{10}\left(\frac{u_9}{u_{10}}\right)^3, \text{ \&c.}$$

Thus the equidistant values of the function to be integrated (arranged backwards) are

$$0, \quad 0, \quad u_8 - u_{10}\left(\frac{u_9}{u_{10}}\right)^2, \quad u_7 - u_{10}\left(\frac{u_9}{u_{10}}\right)^3, \text{ \&c.}$$

The first two are zero, the next three or four are sensible, and the rest are insensible; thus the quadrature is very short. The correction is found to be very small, and we might perhaps have been content with the empirical integral without material loss of accuracy.

§ 17. *The Fifth Zonal Harmonic Inequality.*

This is treated exactly in the same way as the fourth, and I will only give the results.

We have

$$\mathfrak{Q}_5\left(\frac{r}{k}\right) = \frac{8}{7 \cdot 9 \cdot 11} \frac{k^6}{r^6}\left(1 + \tfrac{21}{13}\frac{k^2}{r^2}\right)(1 - 5\beta_0 + \tfrac{385}{16}\beta_0^2),$$

$$\mathfrak{P}_5(\nu) = P_5(\nu) + \tfrac{1}{4}\beta_0 P_5^2(\nu) + \tfrac{1}{128}\beta_0^2 P_5^4(\nu),$$

$$\mathsf{C}_5(\nu) = \sqrt{(1 - \beta_0 \cos 2\phi)}.[1 - 7\beta_0 \cos 2\phi + \tfrac{63}{16}\beta_0^2 \cos 4\phi],$$

$$\mathfrak{T}_5 = 1 + 15\beta_0 + \tfrac{777}{8}\beta_0^2.$$

Whence

$$-\frac{11}{3\lambda\mathfrak{T}_5} \mathfrak{Q}_5\left(\frac{r}{k}\right) \mathfrak{P}_5(1)\, \mathsf{C}_5(\tfrac{1}{2}\pi) = -\frac{8}{189\lambda} \frac{k^6}{r^6}\left(1 + \tfrac{21}{13}\frac{k^2}{r^2}\right)(1 - 13\beta_0 + \tfrac{727}{8}\beta_0^2)\sqrt{(1 + \beta_0)}.$$

Then

$$\mathfrak{P}_5(\nu_0) = \operatorname{cosec}\beta\,(1+a\cot^2\beta+b\cot^2\beta),$$

where

$$a = 7\,(1+\tfrac{15}{4}\beta_0),$$

$$b = \tfrac{63}{8}\,(1+5\beta_0+\tfrac{15}{128}\beta_0^{\,2}).$$

Finally

$$\mathfrak{A}_5 = \kappa\int_0^\gamma\left[\frac{\operatorname{cosec}\beta\,(1+a\cot^2\beta+b\cot^4\beta)}{\operatorname{cosec}\chi\,(1+a\cot^2\chi+b\cot^4\chi)}\right]^2\sec\chi\,d\psi,$$

which is to be evaluated by quadratures as was proposed for the fourth harmonic.

§ 18. *Moment of Momentum and Limiting Stability.*

The moment of momentum of the system is $I\omega$, but when we are determining the configuration of minimum moment of momentum, which is a figure of bifurcation and gives us the configuration of limiting stability, the conditions are different according as whether we are treating the problem of the figures of equilibrium where both masses are liquid, or ROCHE's problem in which the ellipsoid denoted by capital letters is rigid.

Accordingly I write

$$I = \tfrac{4}{3}\pi\rho\mathrm{a}^3\left[\tfrac{1}{5}\frac{\lambda}{1+\lambda}(b^2+c^2)+\frac{\lambda r^2}{(1+\lambda)^2}\right]+\tfrac{4}{3}\pi\rho\mathrm{a}^3\,.\,\tfrac{1}{5}\frac{1}{1+\lambda}(B^2+C^2),$$

and for determining the angular momentum of the figures of equilibrium I take the whole expression for I, but for ROCHE's problem omit the last term.

Since $\omega^2 = \tfrac{4}{3}\pi\rho\dfrac{\mathrm{a}^3}{r^3}(1+\zeta)$, I compute for ROCHE's problem

$$\mu_1 = \frac{\mathrm{a}^{3/2}}{r^{3/2}}(1+\zeta)^{1/2}\left[\tfrac{1}{5}\frac{\lambda}{1+\lambda}\frac{(b^2+c^2)}{\mathrm{a}^2}+\frac{\lambda r^2}{(1+\lambda)^2\,\mathrm{a}^2}\right];$$

and for the figures of equilibrium

$$\mu_2 = \mu_1+\frac{\mathrm{a}^{3/2}}{r^{3/2}}(1+\zeta)^{1/2}\frac{1}{5\,(1+\lambda)}\cdot\frac{B^2+C^2}{\mathrm{a}^2}.$$

The moment of momentum is given by

$$I\omega = (\tfrac{4}{3}\pi\rho)^{3/2}\,\mathrm{a}^5\,(\mu_1 \text{ or } \mu_2).$$

It will be observed that μ_1 and μ_2 are expressible by numbers for any given solution of the problem.

Suppose now that we have a succession of solutions for equidistant values of γ differing but little from one another. Then if the solutions lie close to the region of limiting stability, we shall find that one of them corresponds to minimum moment of momentum, either of μ_1 or of μ_2, as the case may be. Such a solution is a figure of bifurcation, and of the two coalescent solutions one has one more degree of instability than the other. If one of the two is continuous with a stable solution, and if, moreover, in the passage to the undoubtedly stable solution it passes through no other point of bifurcation, one of our two solutions is secularly stable and the other unstable.

Now, two liquid masses revolving about one another orbitally at an infinite distance are undoubtedly stable, and such a case is also continuous with one of our solutions. Further, SCHWARZSCHILD has proved that ROCHE's ellipsoid has no point of bifurcation from first to last, and as this is true of one such ellipsoid, it is true of two.* Hence we conclude that the minima of μ_1 and μ_2 will afford figures of limiting stability.

§ 19. *Approximate Solution of the Problem.*

It is clear that spherical harmonic analysis is applicable to the case when the two liquid masses are widely distant. When they are so much deformed by their interaction that that method becomes inapplicable, good results may be obtained from the formulæ of the last sections by means of development in powers of sin γ, and it is this plan which is especially considered in the present section.

It appears from § 1 that when one of the masses is small compared with the other (λ small), the configuration of limiting stability for the problem of figures of equilibrium occurs when the two masses are very far apart. As λ increases, that configuration corresponds with diminishing radius vector. It seemed then probable that at least some of the solutions might be found by means of these series, and if this were so it might, in many cases, prove unnecessary to follow the same laborious procedure as in finding the limiting stability of ROCHE's ellipsoid. This view was found to be correct, and I therefore think it well to record the methods by which the developments may be obtained, without however giving the full details of the very laborious analysis.

When the masses are far apart, the terms denoted ϵ and η in the equation for κ'^2 and in that for a^3/r^3 are small, and they must be neglected in the developments.

Writing for brevity $g = \sin\gamma$, we may prove that

$$\Omega = \frac{1}{\sin\gamma}\log_e\frac{1+\sin\gamma}{\cos\gamma} = \sum_0^\infty \frac{g^{2n}}{2n+1}, \quad \tan^2\gamma = -1+\sum_0^\infty g^{2n}, \quad \tan^4\gamma = 1+\sum_0^\infty (n-1)\, g^{2n},$$

$$\tan^6\gamma = -1+\sum_0^\infty \frac{(n-1)(n-2)}{1.2}g^{2n}, \quad \tan^8\gamma = 1+\sum_0^\infty \frac{(n-1)(n-2)(n-3)}{1.2.3}g^{2n}, \text{ \&c.}$$

Hence the developments may be obtained of the functions $\sigma_0, \sigma_1, \sigma_2 \ldots \tau_0, \tau_1, \tau_2 \ldots$, and thence of $v_0, v_1, v_2 \ldots$ in series proceeding by powers of g^2; and thence we may find κ'^2 in that form.

---

* SCHWARZSCHILD, "Die Poincarésche Theorie des Gleichgewichts." 'Neue Annalen der k. Sternwarte München,' Band III, 1896.

The result as far as g^4 is

$$\kappa'^2 = \frac{1+\lambda}{4+\lambda}\left[1-\frac{30}{7(1+\lambda)}g^2-\frac{12(11+26\lambda)}{7^2(1+\lambda)^2}g^4\ldots\right].$$

I have also found the term in g^6, but shall make no use of it.

With this value of κ'^2 or of κ^2, which is $1-\kappa'^2$, we develop the expression for a^3/r^3 in the same manner. The result is :—

$$\frac{\mathrm{a}^3}{r^3} = \tfrac{2}{5}\,\frac{1+\lambda}{4+\lambda}g^2\left[1+\frac{5+\lambda}{7(4+\lambda)}g^2-\frac{88+53\lambda}{7^2(4+\lambda)^2}g^4\ldots\right].$$

By inversion we have

$$g^2 = \sin^2\gamma = \frac{5(4+\lambda)}{2(1+\lambda)}\frac{\mathrm{a}^3}{r^3}-\frac{25(5+\lambda)(4+\lambda)}{2^2.7(1+\lambda)^2}\frac{\mathrm{a}^6}{r^6}+\frac{125(69+2\lambda)(2+\lambda)(4+\lambda)}{2^3.7^2(1+\lambda)^3}\frac{\mathrm{a}^9}{r^9}\ldots.$$

Since $\dfrac{k^3\cos\beta\cos\gamma}{\sin^3\beta} = \dfrac{\lambda}{1+\lambda}\mathrm{a}^3$, it follows that $\dfrac{k^2}{\sin^2\beta} = \left(\dfrac{\lambda}{1+\lambda}\right)^{2/3}\dfrac{\mathrm{a}^2}{(\cos\beta\cos\gamma)^{2/3}}$.

The semi-axes of the ellipsoid are given by

$$\frac{c^2}{\mathrm{a}^2} = \frac{k^2}{\mathrm{a}^2\sin^2\beta} = \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\frac{1}{(\cos\beta\cos\gamma)^{2/3}},\quad \frac{a^2}{\mathrm{a}^2} = \frac{c^2}{\mathrm{a}^2}\cos^2\gamma,\quad \frac{b^2}{\mathrm{a}^2} = \frac{c^2}{\mathrm{a}^2}\cos^2\beta.$$

But $\cos^2\gamma = 1-g^2$, $\cos^2\beta = 1-\kappa^2g^2$, and therefore

$$\frac{c^2}{\mathrm{a}^2} = \left(\frac{\lambda}{1+\lambda}\right)^{2/3}(1-g^2)^{-1/3}(1-\kappa^2g^2)^{-1/3};\quad \frac{a^2}{\mathrm{a}^2} = \left(\frac{\lambda}{1+\lambda}\right)^{2/3}(1-g^2)^{2/3}(1-\kappa^2g^2)^{-1/3};$$

$$\frac{b^2}{\mathrm{a}^2} = \left(\frac{\lambda}{1+\lambda}\right)^{2/3}(1-g^2)^{-1/3}(1-\kappa^2g^2)^{2/3}.$$

Setting apart the factor $[\lambda/(1+\lambda)]^{2/3}$, which is common to all, these three are all expressible in the form, say

$$F = 1+(a_0+a_1\kappa^2)g^2+(b_0+b_1\kappa^2+b_2\kappa^4)g^4+(c_0+c_1\kappa^2+c_2\kappa^4+c_3\kappa^6)g^6+\ldots,$$

where the a_0, a_1, b_0, b_1, &c., have different numerical values according to whichever of the three functions we are treating.

Now the above formula for κ'^2 enables us to write

$$\kappa^2 = A_0+B_0g^2+C_0g^4\ldots,$$

where the forms of A_0, B_0, C_0 are obvious.

Hence we have

$$F = 1+(a_0+a_1A_0)g^2+(b_0+a_1B_0+b_1A_0+b_2A_0^2)g^4$$
$$+(c_0+c_1A_0+c_2A_0^2+c_3A_0^3+b_1B_0+2b_2A_0B_0+a_1C_0)g^6\ldots$$

In this way I find the following expressions for the semi-axes in series proceeding by powers of g^2 or $\sin^2\gamma$:—

$$\left.\begin{aligned}
\frac{c^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1+\frac{7+\lambda}{3\,(4+\lambda)}g^2+\frac{524+223\lambda+14\lambda^2}{3^2.7\,(4+\lambda)^2}g^4\right.\\
&\qquad\left.+\frac{120926+86748\lambda+19428\lambda^2+686\lambda^3}{3^4.7^2\,(4+\lambda)^3}g^6\ldots\right]\\
\frac{a^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1-\frac{5+2\lambda}{3\,(4+\lambda)}g^2-\frac{64+8\lambda+7\lambda^2}{3^2.7\,(4+\lambda)^2}g^4\right.\\
&\qquad\left.-\frac{11122+2460\lambda-1851\lambda^2+196\lambda^3}{3^4.7^2\,(4+\lambda)^3}g^6\ldots\right]\\
\frac{b^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1-\frac{2-\lambda}{3\,(4+\lambda)}g^2-\frac{187+110\lambda-14\lambda^2}{3^2.7\,(4+\lambda)^2}g^4\right.\\
&\qquad\left.-\frac{28492+36723\lambda+14160\lambda^2-686\lambda^3}{3^4.7^2\,(4+\lambda)^3}g^6\ldots\right]
\end{aligned}\right\}\quad(66).$$

It is easy to verify that the product of the three series is unity, as should be the case.

The next step is to substitute for g^2, g^4, g^6 … their values in terms of a^3/r^3 and its powers. In this way I find

$$\left.\begin{aligned}
\frac{c^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1+\frac{5\,(7+\lambda)}{6\,(1+\lambda)}\frac{\mathrm{a}^3}{r^3}+\frac{25\,(419+187\lambda+11\lambda^2)}{2^2.3^2.7\,(1+\lambda)^2}\frac{\mathrm{a}^6}{r^6}\right.\\
&\qquad\left.+\frac{125\,(99848+74769\lambda+16503\lambda^2+488\lambda^3)}{2^3.3^4.7^2\,(1+\lambda)^3}\frac{\mathrm{a}^9}{r^9}\ldots\right]\\
\frac{a^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1-\frac{5\,(5+2\lambda)}{6\,(1+\lambda)}\frac{\mathrm{a}^3}{r^3}+\frac{25\,(11+37\lambda-\lambda^2)}{2^2.3^2.7\,(1+\lambda)^2}\frac{\mathrm{a}^6}{r^6}\right.\\
&\qquad\left.-\frac{125\,(23992+17895\lambda+1587\lambda^2+178\lambda^3)}{2^3.3^4.7^2\,(1+\lambda)^3}\frac{\mathrm{a}^9}{r^9}\ldots\right]\\
\frac{b^2}{\mathrm{a}^2} &= \left(\frac{\lambda}{1+\lambda}\right)^{2/3}\left[1-\frac{5\,(2-\lambda)}{6\,(1+\lambda)}\frac{\mathrm{a}^3}{r^3}-\frac{25\,(157+119\lambda-11\lambda^2)}{2^2.3^2.7\,(1+\lambda)^2}\frac{\mathrm{a}^6}{r^6}\right.\\
&\qquad\left.-\frac{125\,(19114+23673\lambda+11577\lambda^2-488\lambda^3)}{2^3.3^4.7^2\,(1+\lambda)^3}\frac{\mathrm{a}^9}{r^9}\ldots\right]
\end{aligned}\right\}\quad(67).$$

By writing $1/\lambda$ for λ we obtain the formulæ for the axes of the other ellipsoid.

The numerical coefficients increase rather rapidly so that the series are useless unless a/r is small, and accordingly this method fails to give any result for ROCHE's ellipsoid in limiting stability; it is, however, useful for the problem of figures of equilibrium, as already stated.

If we had relied on spherical harmonic analysis, we should only have obtained the terms in a^3/r^3.

In order to obtain the expression for the angular momentum, which has to be a minimum for limiting stability, we must evaluate ζ. Now, from (24) and (15), we have

$$
\begin{aligned}
\zeta = \frac{3}{10r^2}&(2c^2-a^2-b^2+\text{ same in } A,\, B,\, C) \\
&+\frac{3}{56r^4}[3(a^4+b^4)+8c^4-8c^2(a^2+b^2)+2a^2b^2+\text{ same in } A,\, B,\, C], \\
&+\frac{3}{20r^4}[2(A^2a^2+B^2b^2+C^2c^2)+(A^2+B^2+C^2)(a^2+b^2+c^2)-5C^2(a^2+b^2) \\
&\qquad\qquad -5c^2(A^2+B^2)+5c^2C^2].
\end{aligned}
$$

By means of the above series for a^2, b^2, c^2, and of their analogues for A^2, B^2, C^2, I find

$$\zeta = l\frac{\mathrm{a}^5}{r^5}+m\frac{\mathrm{a}^8}{r^8}+n\frac{\mathrm{a}^{10}}{r^{10}},$$

where

$$l = \tfrac{3}{4}\cdot\frac{\lambda^{2/3}(7+\lambda)+7\lambda+1}{(1+\lambda)^{5/3}},$$

$$m = \tfrac{5}{14}\cdot\frac{\lambda^{2/3}(82+38\lambda+\lambda^2)+82\lambda^2+38\lambda+1}{(1+\lambda)^{8/3}},$$

$$n = \tfrac{225}{224}\frac{\lambda^{4/3}(33+10\lambda+\lambda^2)+33\lambda^2+10\lambda+1}{(1+\lambda)^{10/3}}+\tfrac{15}{16}\frac{\lambda^{2/3}(15+102\lambda+15\lambda^2)}{(1+\lambda)^{10/3}}.$$

Now we have to evaluate the moment of momentum given above in § 18, viz.,

$$\mu_2 = \left(\frac{\mathrm{a}}{r}\right)^{3/2}(1+\zeta)^{1/2}\left[\tfrac{1}{5}\frac{\lambda}{1+\lambda}(b^2+c^2)+\tfrac{1}{5}\frac{1}{1+\lambda}(B^2+C^2)+\frac{\lambda}{(1+\lambda)^2}r^2\right].$$

When b^2, c^2, B^2, C^2, have their values attributed to them, we find

$$\mu_2 = \frac{\lambda}{(1+\lambda)^2}\left(\frac{\mathrm{a}}{r}\right)^{3/2}(1+\zeta)^{1/2}\left[R+S\frac{\mathrm{a}^3}{r^3}+T\frac{\mathrm{a}^6}{r^6}+U\frac{\mathrm{a}^9}{r^9}\ldots+r^2\right],$$

where

$$R = \frac{2}{5\lambda}(1+\lambda^{5/3})(1+\lambda)^{1/3},$$

$$S = \frac{1}{6(1+\lambda)^{2/3}}\left[\lambda^{2/3}(5+2\lambda)+\frac{1}{\lambda}(5\lambda+2)\right],$$

$$T = \frac{5}{2.3^2.7\,(1+\lambda)^{5/3}}\left[\lambda^{2/3}(131+34\lambda+11\lambda^2)+\frac{1}{\lambda}(131\lambda^2+34\lambda+11)\right],$$

$$
\begin{aligned}
U = \frac{25}{2^2.3^4.7^2\,(1+\lambda)^{8/3}}\Big[&\lambda^{2/3}(40367+25548\lambda+2463\lambda^2+488\lambda^3) \\
&+\frac{1}{\lambda}(40367\lambda^3+25548\lambda^2+2463\lambda+488)\Big].
\end{aligned}
$$

In § 1, where the same problem is treated for two spheres, we had l, m, n, S, T, U, all zero.

In order to find the minimum moment of momentum for a given value of λ, I compute l, m, n, R, S, T, U, and assuming several equidistant values of r compute values of $\mu_2 \times \frac{(1+\lambda)^2}{\lambda}$. When the coefficients are computed we very easily find the value of r corresponding to the minimum.

When that value of r is found, we are in a position to compute the axes of the two ellipsoids.

For values of λ less than $\frac{1}{2}$ the results found in this way would be satisfactory, and for $\lambda = \frac{1}{2}$ they are, I think, adequate. Even for the case of $\lambda = 1$ the result is not very remote from the truth, for whereas the correct result for the minimum of angular momentum is $r/a = 2{\cdot}638$, the result derived from this approximate method is $r/a = 2{\cdot}51$. But it would have been impossible to foresee that the result would be as good as it is.

PART II.—NUMERICAL SOLUTIONS.

§ 20. ROCHE'S *Infinitesimal Ellipsoidal Satellite in Limiting Stability.*

We require to find the form of an infinitesimal satellite (so that $\lambda = 0$) revolving in a circular orbit about a *spherical* planet. When this problem is solved we shall be able to see how far the solution will be affected when we allow the spherical planet to become oblate under the influence of a rotation of the same speed as that of the revolution of the infinitesimal satellite. This last is what I have called the modified form of ROCHE'S problem.

The planet being spherical and λ being zero, the small terms ζ, ϵ, η vanish, so that our solution becomes rigorous.

The angular momentum of the planet's axial rotation is to be omitted, and the satellite being infinitesimal the momentum of its axial rotation is zero. Thus the moment of momentum of the system varies as the square root of the satellite's radius vector, and minimum momentum coincides with minimum radius vector.

The solution of the problem has been obtained in two ways: first by LEGENDRE'S tables of elliptic integrals, and secondly by means of the auxiliary tables given above. In the first method, I knew with fair approximation by various preliminary computations the values of κ and γ which lay near to the required solution. Now there is a certain function of κ, γ, say $f(\sin^{-1}\kappa, \gamma)$, which vanishes when the ellipsoid is a figure of equilibrium; accordingly I computed by means of LEGENDRE'S tables the following eight values of $f(\sin^{-1}\kappa, \gamma)$ for integral degrees of $\sin^{-1}\kappa$ and γ:—

$$f(77°, 57°) = +0{\cdot}0000878, \quad f(77°, 58°) = -0{\cdot}0000624$$
$$f(78°, 59°) = +0{\cdot}0000724, \quad f(78°, 60°) = -0{\cdot}0000785$$
$$f(79°, 61°) = +0{\cdot}0000562, \quad f(79°, 62°) = -0{\cdot}0000939$$
$$f(80°, 63°) = +0{\cdot}0000408, \quad f(80°, 64°) = -0{\cdot}0001046$$

(probably the last significant figure in each of these is inaccurate).

Interpolating from these we find four values satisfying $f(\sin^{-1}\gamma, \kappa) = 0$, namely:—

$$f(77°, 57°{\cdot}5846) = 0,\ f(78°, 59°{\cdot}4798) = 0,\ f(79°, 61°{\cdot}3744) = 0,\ f(80°, 63°{\cdot}2806) = 0.$$

With these solutions I find

$\sin^{-1}\kappa$	r/a
77°	2·467860
78°	2·458191
79°	2·455446
80°	2·460289

By formulæ of interpolation the minimum of r occurs when $\sin^{-1}\kappa = 78°{\cdot}8756$. Then by a second interpolation this value of κ corresponds with $\gamma = 61°{\cdot}1383$, and the minimum value of r is 2·45539. We may take then $\gamma = 61°\ 8'{\cdot}3$, $\kappa = \sin 78°\ 52'{\cdot}5$, whence $\beta = 59°\ 14'{\cdot}5$. Since $\cos\gamma = 0{\cdot}4827$, $\cos\beta = 0{\cdot}5114$, the three axes of the ellipsoid are proportional to 10000, 5114, 4827; Roche gave the ratios 1000, 496, 469, and the radius vector as 2·44, in place of 2·45539.

Turning now to the second solution, I solved the problem by means of the auxiliary tables in two ways, namely, for $\gamma = 60°, 61°, 62°$ and also for $\gamma = 57°, 59°, 61°, 63°$.

They led to virtually identical results, viz., that the minimum of r is 2·45521, corresponding to $\gamma = 61°\ 8'{\cdot}4$, $\sin^{-1}\kappa = 78°\ 52'{\cdot}0$.

Finally the solution for Roche's limit and for the ratio of the axes of the ellipsoid in limiting stability may be taken to be as follows:—

γ	$\sin^{-1}\kappa$	$\cos\gamma$	$\cos\beta$	r/a
$61°\ 8\frac{1}{2}'$	78° 52′	0·4827	0·5114	2·4553,

with uncertainty of unity in the last place of decimals in r and of half a minute of arc in $\sin^{-1}\kappa$.

We must next consider the modified form of Roche's problem, in which the large body or planet yields to centrifugal force and becomes an oblate ellipsoid of revolution. The approximate formulæ of § 19 show that when $\lambda = \infty$ or when $\lambda = 0$,

$$l = \tfrac{3}{4},\quad m = \tfrac{5}{14},\quad n = \tfrac{225}{224}.$$

Hence in this case

$$\zeta = \tfrac{3}{4}\left(\frac{a}{r}\right)^5 + \tfrac{5}{14}\left(\frac{a}{r}\right)^8 + \tfrac{225}{224}\left(\frac{a}{r}\right)^{10} \ldots.$$

The solution of the modified problem can only differ slightly from that just found when the planet is spherical, and therefore we may compute ζ with sufficient accuracy by means of the values of a/r already found. I accordingly computed ζ for $\gamma = 60°, 61°, 62°$, and found that in each case ζ was very nearly equal to 0·0088.

Now it is proved in the footnote to § 10 that, when $\lambda = 0$ and when the planet yields to centrifugal force, $\epsilon = \eta = \zeta$; as the value of ζ is found with good approximation, it is easy to compute r for these three values of γ. I thus find that in the modified problem, minimum radius vector, and therefore limiting stability, occurs when $r = 2{\cdot}457$, $\gamma = 61^\circ\ 12'$, $\kappa = \sin 78^\circ\ 50'$, $\beta = 59^\circ\ 17'$; the axes of the large body are determined by the approximate formulæ of § 10 to be $\frac{C}{\mathrm{a}} = \frac{B}{\mathrm{a}} = 1{\cdot}0304$, $\frac{A}{\mathrm{a}} = 0{\cdot}9418$.

It appears then that the yielding of the planet to centrifugal force makes very little difference, as was to be expected.

These results are included in the table given below of results for solutions of the modified problem of ROCHE with finite values of λ.

§ 21. ROCHE'S *Ellipsoidal Satellite, of finite mass, in limiting stability, the planet being also ellipsoidal.*

This is the problem which I describe as the "modified" problem of ROCHE. It seemed unnecessary to carry out the computations for the smaller values of λ, since they are sufficiently represented by the case of the infinitesimal satellite where λ is zero. I therefore begin with the case of $\lambda = 0{\cdot}4$ and pass on to $\lambda = 0{\cdot}5$, 0·6, 0·7, 0·8, 0·9, 1·0.

It seems well to describe the process followed in one case as a type of all. It was, in general, possible either by extrapolation from neighbouring values of λ, or by mere guessing, to begin with some values of ζ, ε, η and their co-relative functions E, H for the larger body, which were somewhere near the truth. With these we could compute r, κ, Γ, K with fair approximation; thence values of ζ, ε, η, E, H could be calculated with close accuracy and the computation could be repeated. It was, of course, a matter of conjecture as to what initial values of γ would be found to embrace the region of minimum angular momentum.

I will now describe the process for $\lambda = 0{\cdot}4$. Passing over the preliminary stages in which fairly good values were found, we begin with the following conjectural values:—

γ.	46°.	48°.	50°.	Γ.	32°.	34°.	36°.
$\sin^{-1}\kappa$	68° 24′·8	69° 32′·0	70° 41′·3	$\sin^{-1}K$	50° 12′·0	51° 18′·8	52° 34′·9
Γ	33° 13′·9	34° 18′·8	35° 18′·5	γ	43° 50′·9	47° 24′·4	51° 34′·1
$\sin^{-1}K$	50° 52′·0	51° 30′·1	52° 7′·5	$\sin^{-1}\kappa$	67° 15′·0	69° 11′·8	71° 37′·0
$\log r$	0·40245	0·39594	0·39060	$\log r$	0·41071	0·39775	0·38726,

whence I compute

ζ	0·056259	0·064863	0·074219	ζ	0·047883	0·062231	0·082010
ϵ	0·045435	0·048102	0·050256	E	0·140179	0·174168	0·218540
η	0·32004	0·36426	0·40838	H	0·40539	0·52564	0·69272.

By means of these and the auxiliary tables I find

$\sin^{-1}\kappa$	68° 24′·6	69° 31′·8	70° 40′·5	$\sin^{-1}K$	50° 11′·8	51° 18′·8	52° 33′·8
$\log r$	0·40240	0·39591	0·39046	$\log r$	0·41068	0·39768	0·38693.

The computed values are so very close to the conjectural ones, in so far as they have been as yet computed, that we might be content, but in order to illustrate the process when the conjectures are less satisfactory, I proceed to the next stage.

By far the greater part of the discrepancy between assumed and computed values (which in some cases was considerable) arises from error in the assumed values of r. Now assuming κ and K to be correct, it is very easy to correct the results for a changed value of r.

In this case I find

corrected ζ	0·056274	0·064873	0·074271	corrected ζ	0·047890	0·062253	0·082137
,, ϵ	0·04545	0·04811	0·05030	,, E	0·14020	0·17423	0·21889
,, η	0·32012	0·36431	0·40867	,, H	0·40546	0·52583	0·69385

Recomputing

$\sin^{-1}\kappa$	unchanged			$\sin^{-1}$ K	unchanged		
corrected $\log r$	0·40240	0·39591	0·39047	corrected $\log r$	0·41069	0·39768	0·38695.

By means of these we find two formulæ of interpolation, namely :—

$$\frac{r}{a} = 2\cdot4884 - 0\cdot0342\left(\frac{\gamma-48^\circ}{2}\right) + 0\cdot0032\left(\frac{\gamma-48^\circ}{2}\right)^2,$$

$$\frac{r}{a} = 2\cdot4985 - 0\cdot0685\left(\frac{\Gamma-34^\circ}{2}\right) + 0\cdot0075\left(\frac{\Gamma-34^\circ}{2}\right)^2.$$

These two expressions may be equated to one another, and therefore we have the means of finding simultaneous values of γ and Γ, and thence by another formula of interpolation of κ and K. Hence I obtain

γ.	46°.	48°.	50°.	Γ.	32°.	34°.	36°.
Γ	33° 13′·4	34° 17′·9	35° 17′·4	γ	43° 47′·4	47° 25′·4	51° 34′·4
$\sin^{-1}$ K	50° 52′·2	51° 29′·5	52° 6′·3	$\sin^{-1}\kappa$	67° 12′·1	69° 12′·3	71° 35′·6.

Comparison with the initial values shows that the conjectures were very good.

It now remains to compute the moment of momentum, and as we are dealing with ROCHE'S problem the rotational momentum of the larger ellipsoid is not required. It follows that the values of Γ and K are not used, and since they are only required for finding the shape of the larger ellipsoid, there was no necessity for a high degree of accuracy in them. The moment of momentum is represented by the quantity μ_1 of § 18. I find then

γ.	46°.	48°.	50°.
μ_1	0·348640	0·348300	0·348519.

By formulæ of interpolation the minimum value occurs when $\gamma = 48^\circ\ 12'\cdot9$ and $\kappa = \sin\ 69^\circ\ 39'\cdot1$. The corresponding values are $\frac{r}{a} = 2\cdot4848$, $\Gamma = 34^\circ\ 25'\cdot6$, K = sin 51° 33′·5. The last step is to compute the axes of the two ellipsoids from the values of κ, γ, K, Γ.

Of course the numbers set out above make no claim to absolute accuracy, but the results tabulated below are, I believe, substantially correct.

The unit of length employed is the radius of a sphere whose mass is equal to the mass of the whole system. If it were preferred to express the results in terms of the mean radius of the larger body, all linear results would have to be multiplied by $(1+\lambda)^{1/3}$.

We may now collect the results in a tabular form, as follows :—

Solutions for Roche's Ellipsoid in Limiting Stability.

The unit of length is the radius of a sphere whose mass is equal to the sum of the masses, *i.e.*, $abc+ABC = 1$, and $\dfrac{abc}{ABC} = \lambda$.

λ.	γ.	sin⁻¹ κ.	a.	b.	c.	Γ.	sin⁻¹ K.	A.	B.	C.	r.
0	61° 12′	78° 50′	0·482÷ ∞	0·511÷ ∞	1·0 ÷ ∞	—	—	0·942	1·030	1·030	2·457
0·4	48° 13′	69° 39′	0·562	0·603	0·843	34° 25′	51° 34′	0·815	0·886	0·988	2·485*
0·5	46° 40′	68° 12′	0·597	0·642	0·870	35° 59′	54° 30′	0·792	0·860	0·979	2·484
0·6	45° 5′	66° 43′	0·627	0·674	0·888	37° 14′	56° 41′	0·772	0·836	0·969	2·490
0·7	43° 38′	65° 20′	0·652	0·701	0·901	38° 9′	58° 18′	0·753	0·815	0·958	2·497
0·8	42° 26′	64° 4′	0·673	0·725	0·912	38° 57′	59° 39′	0·737	0·796	0·947	2·502
0·9	41° 25′	62° 58′	0·691	0·744	0·921	39° 40′	60° 47′	0·722	0·778	0·937	2·508
1·0	40° 15′	61° 43′	0·708	0·762	0·927	40° 15′	61° 43′	0·708	0·762	0·927	2·514

The cases λ = 0·4, 0·7, 1·0 are illustrated by figs. 2, 3, 4. The meaning of the dotted lines near the vertices of the smaller ellipsoid will be explained in the next section.

The distance $r-(c+C)$ is the interval between the vertices of the two ellipsoids; the following are the values, using, however, more places of decimals than are tabulated above :—

λ.	$r-(c+C)$.	λ.	$r-(c+C)$.
0	1·030	0·7	0·638
0·4	0·653	0·8	0·643
0·5	0·635	0·9	0·650
0·6	0·633	1·0	0·660

It is remarkable how very nearly constant the intervening space remains throughout a large range in the values of λ.

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[*] The values $r = 2·485$ for $\lambda = 0·4$ and $r = 2·484$ for $\lambda = 0·5$ represent 2·4848 and 2·4844 respectively; it is probable that the last significant figure in the former is a little too large and in the latter too small, and that it might have been more correct to invert the 2·485 and 2·484 in the table. I give the result, however, of the computation.

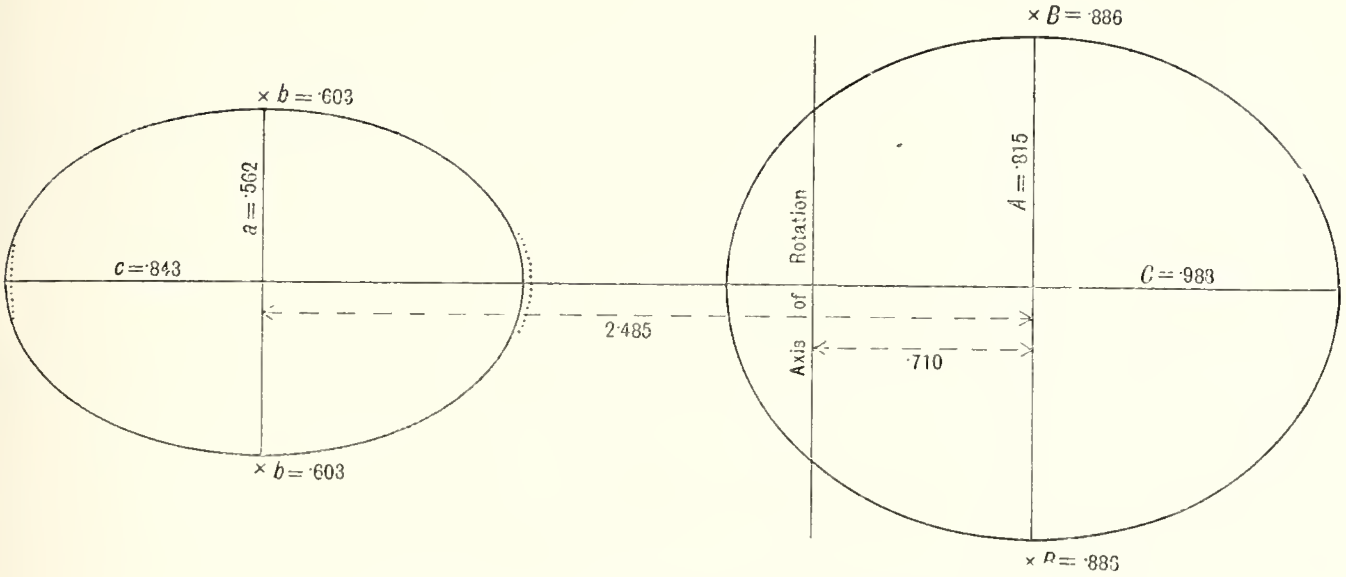

Fig. 2. ROCHE's ellipsoid in limiting stability, when $\lambda = 0 \cdot 4$.

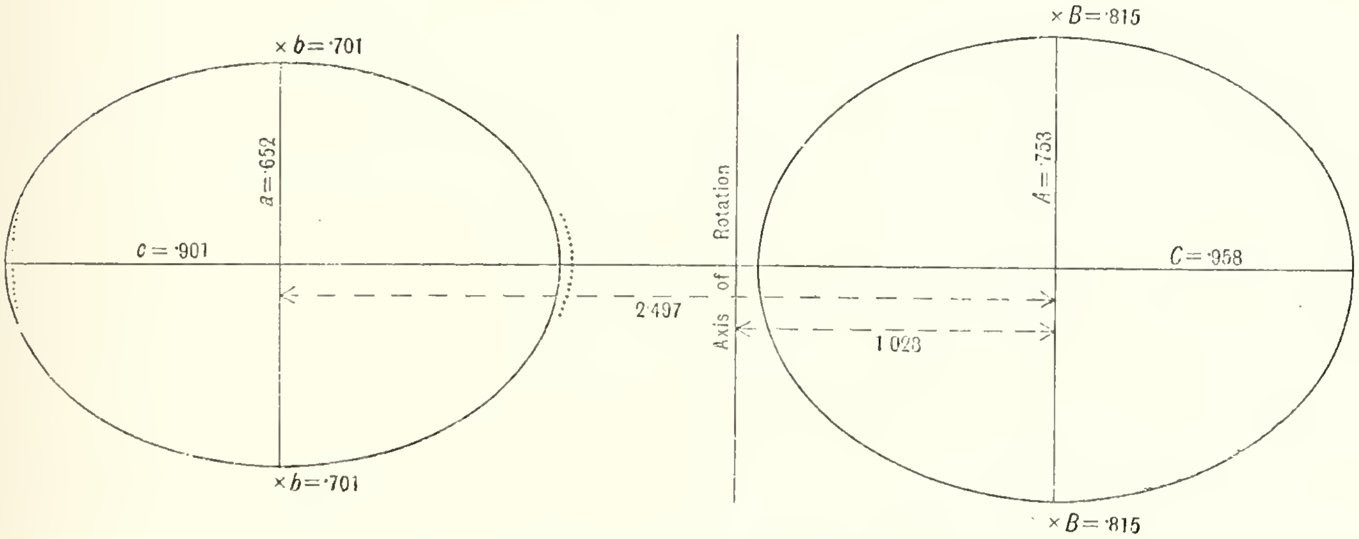

Fig. 3. ROCHE's ellipsoid in limiting stability, when $\lambda = 0 \cdot 7$.

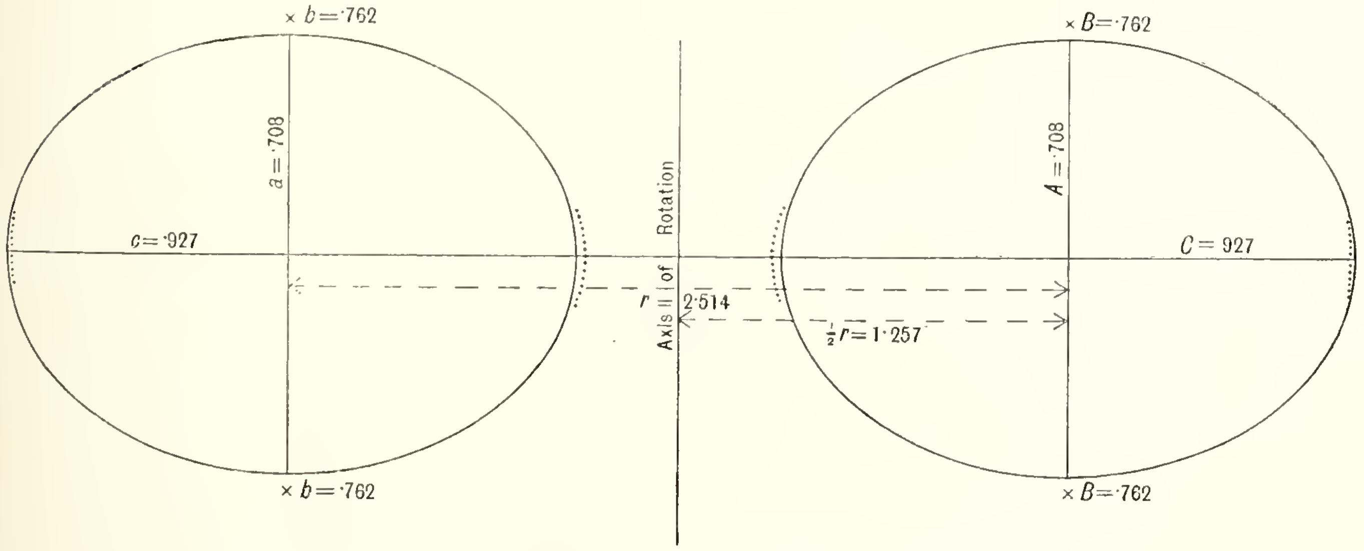

Fig. 4. ROCHE's ellipsoids in limiting stability for equal masses.

§ 22. *Harmonic Deformations of the Ellipsoids.*

When λ is infinitely small, so that the liquid satellite is infinitely small, the harmonic deformations are evanescent, and the same is true when λ is infinitely great. We saw in § 14 that there was reason to suppose that ROCHE's ellipsoid in limiting equilibrium might be more markedly deformed for values of λ midway between zero and unity than for the latter value. I therefore determined the harmonic deformations in the three cases $\lambda = 0{\cdot}4,\ 0{\cdot}7,\ 1{\cdot}0$.

The formulæ for the ellipticities f_3, f_3^2, f_4, f_5 are given in §§ 14, 16, 17 and their values may be found for the ellipsoids in limiting stability tabulated in the last section. It appears that in every case the amount of deformation is small, and therefore it was sufficient to compute the normal deformation at the two extremities of the c semi-axis, that is to say, at the points nearest to and most remote from the other ellipsoid. At these points the normal displacement outwards may be denoted δc, with numbers affixed thereto so as to indicate to which harmonic it is due.

The results may be given in a tabular form, but it may be well to remark that f_3^2 (second tesseral of the third harmonics) was only computed in two instances, because its effect was obviously quite negligible. For the same reason f_4^2, f_4^4, f_5^2, f_5^4 were not computed at all. The following are the computed values of the ellipticities :—

λ.	0·4.	0·7.	1·0.
f_3	0·161	0·234	0·163
f_3^2	−0·127	−0·102	?
f_4	0·0042	0·0066	0·0059
f_5	0·0009	0·0024	0·0033

We saw reason to suppose that the higher harmonics would be relatively more important for the larger values of λ, and there is evidence of the general correctness of this view.

The values of the ellipticities afford us no idea of the amount of the normal correction, and I therefore proceed to tabulate the values of δc, the prolongations of the c semi-axis.

Towards larger ellipsoid

λ.	0·4.	0·7.	1·0.
δc_3	0·0193	0·0283	0·0194
$\delta c_3{}^2$	0·00039	0·00068	?
δc_4	0·00472	0·00886	0·00911
δc_5	0·00110	0·00384	0·00629
Total δc	0·0255	0·0417	0·0348
c	0·8433	0·9006	0·9270
$c+\delta c$	0·8688	0·9423	0·9618
$\dfrac{\delta c}{c}$	1/33	1/22	1/27

Away from larger ellipsoid

λ.	0·4.	0·7.	1·0.
δc_3	−0·0193	−0·0283	−0·0194
$\delta c_3^{\,2}$	−0·00039	−0·00068	?
δc_4	+0·00472	+0·00886	+0·00911
δc_5	−0·00110	−0·00384	−0·00629
Total δc	−0·0161	−0·0240	−0·0166
c	0·8433	0·9006	0·9270
$c+\delta c$	0·8272	0·8766	0·9104
$\frac{\delta c}{c}$	1/52	1/37	1/56

The last line in each division of this table has been given in order to show the relative importance of the total correction. It is clear that the ellipsoid remains a substantially correct solution.

These corrections to the semi-major axes are indicated by dotted lines at the extremities of the longest axis of the smaller mass in figs. 2 and 3, and of both masses in fig. 4.

We have in the last section tabulated $r-(c+C)$, the distance between the two vertices. Now, although I have not calculated the deformations of the larger ellipsoid, it is pretty clear that they must bear to those of the smaller one approximately the ratio of λ to unity. Accepting this conjecture, we have for the δC of the larger ellipsoid towards the smaller one the following values :—

λ.	0·4.	0·7.	1·0.
δC	0·010	0·029	0·035

The distance between the two surfaces of liquid is clearly $r-(c+\delta c+C+\delta C)$.

Thus we have

λ.	0·4.	0·7.	1·0.
$r-(c+C)$	0·653	0·638	0·660
$\delta c+\delta C$	0·036	0·071	0·070
$r-(c+\delta c+C+\delta C)$	0·617	0·567	0·590

§ 23. *Certain Tests and Verifications.*

In order to test how nearly the solution for a^3/r^3 by series in (40) of § 11 would agree with the solution (36) of § 10 in terms of the F elliptic integral, I computed for $\lambda = 0·7$ the value of r/a in the two ways for three values of γ, and found the following results :—

$\lambda = 0·7$.

γ.	42°.	44°.	46°.
r/a by series	2·5355	2·4888	2·4500
r/a by elliptic integrals	2·5359	2·4881	2·4495

The agreement seems to be as close as could be expected when five-figured logarithms are used.

Certain terms in ζ, as expressed in (24) of § 10, were neglected on the ground that they are of higher order than those retained. But it appears from the approximate solution in § 19 that the coefficients of the terms retained are themselves small, so that we are really only retaining terms of the same order as others which are neglected.

The most important of the neglected terms in ζ is

$$-\frac{3}{k} f_3 \mathfrak{P}_3(\nu_0)\, \mathfrak{P}_3(1)\, \mathsf{C}_3(\tfrac{1}{2}\pi)\, r^2 \frac{d}{dr} \mathfrak{Q}_3\left(\frac{r}{k}\right),$$

and this is a term of the seventh order. It seems, therefore, well to compute this in one case, and see how large a proportion it bears to the whole value.

Since

$$\mathfrak{Q}_3\left(\frac{k}{r}\right) = \frac{k^4}{7\kappa^2 r^4}\left(1 + \tfrac{10}{9}\frac{k^2}{\kappa r^2}\right),$$

$$r^2 \frac{d}{dr} \mathfrak{Q}_3\left(\frac{k}{r}\right) = -\frac{4k^4}{7\kappa^2 r^3}\left(1 + \tfrac{5}{3}\frac{k^2}{\kappa r^2}\right).$$

Using this value and the other approximate values given in § 14, where f_3 is determined, I find that the neglected term is

$$\frac{-\dfrac{4}{7\lambda}\dfrac{\Delta_1{}^4}{\sin^6\beta}\left(1 + 0\kappa'^2 - \tfrac{15}{16}\kappa'^4\right)\dfrac{k^7}{r^7}\left(1 + \tfrac{25}{9}\dfrac{k^2}{\kappa r^2}\right)}{\mathfrak{A}_3 - \mathsf{A}_1{}^1 - \dfrac{k^3}{3\lambda r^3}\dfrac{\cos^2\gamma}{\sin^2\beta}\left(1 + \dfrac{3\,(3+\kappa^2)}{14\kappa^2}\dfrac{k^2}{r^2}\ldots\right)}.$$

The numerical value of this, for the case of ROCHE's ellipsoid in limiting stability when $\lambda = 0{\cdot}7$, is found to be $+0{\cdot}0016$. Now, the value of ζ, as computed from the terms retained, was found to be $0{\cdot}0677$. Thus the neglected term is about one 42nd of the whole. The neglect then seems fairly justified.

I thought it worth while to discover how far the modification of ROCHE's problem, whereby the larger body is ellipsoidal, affects the result. I find that whereas it makes but little difference in the solution for any single assumed value of γ, it does make a sensible difference in the incidence of the minimum of angular momentum, and therefore of limiting stability. Thus, when $\lambda = 0{\cdot}5$, I found in one of my preliminary solutions for ROCHE's modified problem that limiting stability occurs when $r/a = 2{\cdot}49$ (the more correct value is $2{\cdot}484$), but when the larger body is a sphere it occurs when $r/a = 2{\cdot}35$. Thus we see that ellipticity in the larger body induces instability at a greater distance than if it were spherical. This might have been conjectured from general considerations.

§ 24. *Figures of Equilibrium of Two Masses in Limiting Stability.*

In this case both masses are liquid. We saw in § 2 that when one of the masses is infinitely small, stability only exists when the two are infinitely far apart. When λ is less than $0\cdot5$ we may obtain fair results from the approximate investigation of § 19, but for greater values of λ it is necessary to employ the laborious method adopted in determining ROCHE's ellipsoid.

When $\lambda = 0\cdot5$ I obtain the following approximate results for the two figures :—

$$r = 2\cdot574$$

$$\begin{array}{ll} a = 0\cdot62, & A = 0\cdot81, \\ b = 0\cdot66, & B = 0\cdot87, \\ c = 0\cdot81, & C = 0\cdot95. \end{array}$$

It is probable that the value of r derived in this way is too small.

For $\lambda = 0\cdot4$, I found $r = 2\cdot59$, but did not calculate the axes.

The only other case in which the problem has been solved is for equal masses, when $\lambda = 1$. The two ellipsoids are exactly alike, and I find limiting stability occurs for the following values :—

$$\gamma = 36^\circ\ 18', \quad \kappa = \sin 59^\circ\ 33', \quad r = 2\cdot638, \quad a = 0\cdot723, \quad b = 0\cdot771, \quad c = 0\cdot897\,;$$

and

$$r - 2c = 0\cdot844.$$

This is illustrated in fig. 5.

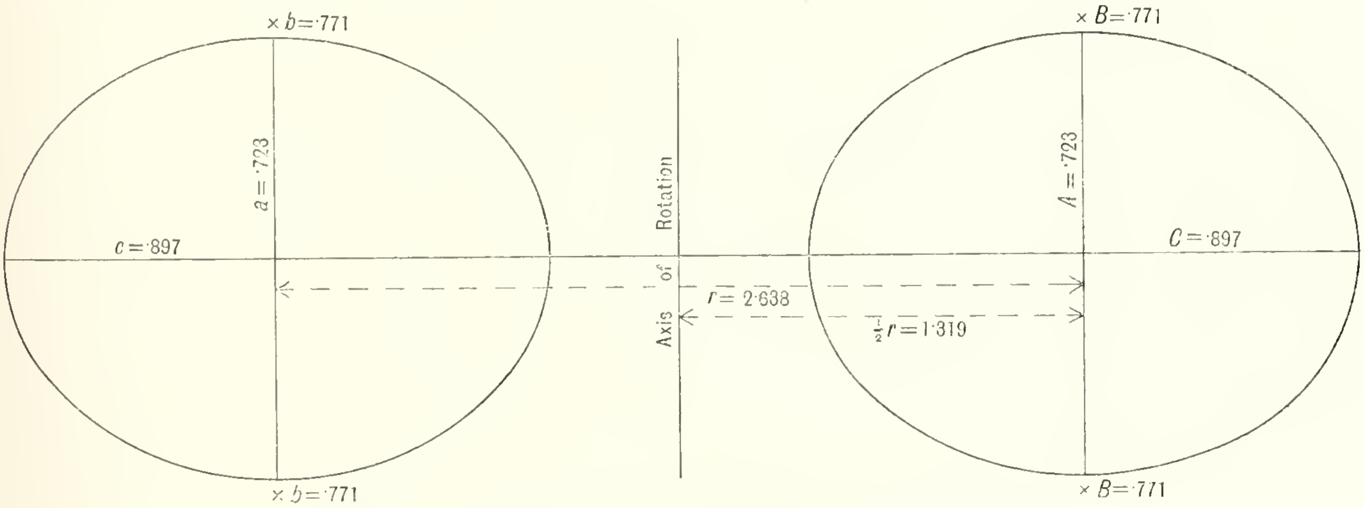

Fig. 5. Two equal masses of liquid in limiting stability.

§ 25. *Unstable Figures of Equilibrium of Two Masses.*

When $\lambda = 0$ the figure of minimum radius vector, when the larger body is rigid, is also that of minimum angular momentum, but for larger values of λ there is an ellipsoid considerably nearer to the larger body than that which possesses limiting stability. I have only determined the ellipsoid of minimum radius vector in two cases, viz., when $\lambda = 0{\cdot}8$ and $1{\cdot}0$.

When $\lambda = 0{\cdot}8$ I find minimum radius vector to be $r = 2{\cdot}36$, whereas limiting stability occurs for $r = 2{\cdot}50$. When $\lambda = 0{\cdot}8$, $r = 2{\cdot}36$, the ellipsoids are determined by the following data :—

$$\gamma = 54^\circ\ 20', \quad \kappa = \sin 71^\circ\ 51', \quad \Gamma = 46^\circ\ 10', \quad K = \sin 64^\circ\ 20' ;$$

whence

$$a = 0{\cdot}619, \qquad A = 0{\cdot}705,$$
$$b = 0{\cdot}675, \qquad B = 0{\cdot}774,$$
$$c = 1{\cdot}063, \qquad C = 1{\cdot}018.$$

When $\lambda = 1$, the minimum radius vector occurs when γ is about 54° and is then equal to $2{\cdot}343$, whereas limiting stability occurs when $r = 2{\cdot}514$. I have not computed the axes, since it suffices to learn that there is an ellipsoidal solution when the two masses are considerably nearer than is consistent with stability.

As γ increases, the ellipsoids get longer and longer, and it is interesting to inquire whether they increase in length with such rapidity that, notwithstanding the increase of r, the interval between the two vertices continues to decrease, or whether the increase of r annuls the simultaneous increase of c.

The following table of values, computed with fair but not extreme accuracy, affords the answer to this question.

$\lambda = 1$.

γ.	r.	c.	$r-2c$.	Differences.
44°	2·429	0·962	0·506	
				−76
46°	2·396	0·983	0·430	
				−74
48°	2·370	1·007	0·356	
				−70
50°	2·354	1·034	0·286	
				−69
52°	2·345	1·064	0·217	
				−68
54°	2·343	1·097	0·149	
				−67
56°	2·350	1·134	0·082	
				−67
58°	2·367	1·176	0·015.	

The differences of $r-2c$ hardly diminish at all, and it is clear that the next entry would be negative, or in other words the two figures would overlap.

These results are obtained on the supposition that our approximation is adequate, but the small terms ζ, ϵ, η, which are really infinite series, show signs of bad convergence as γ increases. I think it probable that when we get to these extreme cases the convergence breaks down. It appears, however, justifiable to argue from these results that the unstable body continually elongates until its end coalesces with the other elongated body. I have no doubt but that the same holds true when the masses are unequal, and that we should always find $r-(c+C)$ diminishing until the two meet. The poorness of the approximation of course would prevent us from making good drawings when coalescence is approaching.

§ 26. *On the Possibility of Joining the Two Masses by a Weightless Pipe.*

This subject is considered in § 13, and it is there shown that if a certain function written $f(\mathrm{a}/r)$, for a given solution of the figures of equilibrium of two detached masses of liquid, is positive, the two masses are too far apart to admit of equilibrium when joined by a pipe without weight—and conversely.

Now I have computed $f(\mathrm{a}/r)$ in a number of cases of ROCHE's ellipsoids in limiting stable equilibrium, and have found it always to be decisively positive.

The corresponding function for two spheres is given in (3) of § 3, and its first term is $+\mathrm{a}^3/r^3$. When we compute it for two ellipsoids, we find the corresponding term to have become negative, and the additional terms, which are given in (44), § 13, are also negative. Hence $f(\mathrm{a}/r)$ is decidedly less for two ellipsoids than it is for two spheres of the same masses with the same radius vector. Thus the deformation of the two bodies tends in the direction of making it possible to join them by a pipe without weight, but it seems certain that in the cases of the ROCHE's ellipsoids in limiting stability such junction remains impossible.

I also computed $f(\mathrm{a}/r)$ for the much elongated ellipsoids which are roughly computed in the last section and finally overlap, and always found $f(\mathrm{a}/r)$ to be positive, as far as the approximate formula went. The additional terms tend, however, more and more to cause $f(\mathrm{a}/r)$ to vanish, and the approximation becomes very imperfect. Now I believe, although I cannot prove it rigorously, that if we could obtain a more exact evaluation of the forms of these elongated ellipsoids, and if further a more exact value of $f(\mathrm{a}/r)$ were calculable, we should find $f(\mathrm{a}/r)$ vanishing near the stage when the computations would show the two ellipsoids to overlap. It therefore seems probable that there is a figure of equilibrium consisting of two elongated masses joined by a narrow neck. These ellipsoids are very unstable when detached, and, according to the principles of § 2, it seems inconceivable that junction by a neck of fluid could render them stable.

PART III.—SUMMARY.

Since the foregoing investigation may be read by mathematicians, while astronomers and physicists will perhaps wish to learn the nature of the conclusions arrived at, I shall devote this part of the paper to a general discussion of the subject, without reference to the mathematical processes used.

Two problems are solved here simultaneously; for the analysis required for their solutions is almost identical, although the principles involved are very distinct.

We conceive that there are two detached masses of liquid in space which revolve about one another in a circular orbit without relative motion—just as the moon revolves about the earth; the determination of the shapes assumed by each mass, when in equilibrium, is common to both our problems. It is in the conditions which determine secular stability that the problem divides itself into two.

One cause of instability in the system resides in the effect on each body of the reaction on it of the frictionally resisted tides raised by it in the other. If now the larger of the two masses were rigid, while still possessing the same shape which it would have had if formed of liquid, the only effect on the orbital stability of the system would be due to the friction of the tides of the smaller mass generated by the attraction of the larger one. Investigation shows that in this case, as the two masses are brought nearer and nearer together, instability would not supervene from tidal friction until the two masses were almost in contact; but it is clear that the deformation of the figure of the liquid mass presents another possible cause of instability. In fact, instability, as due to the deformation of figure, will set in when the masses are still at a considerable distance apart. It amounts to exactly the same whether we consider the larger mass to be rigid, or whether we treat it as liquid and agree to disregard the instability which arises from the friction of the tides raised in it by the smaller body. Accordingly we may describe the stability just considered as "partial," whilst full secular stability of both bodies will depend on the tidal friction of the larger mass also.

The determination of the figure and partial stability of a liquid satellite (*i.e.*, apart from the effects of the tidal friction of the planet) is the problem of ROCHE. He, however, virtually regarded the planet as constrainedly a sphere, whilst in general I have treated it as an ellipsoid with the form of equilibrium.

It has already been remarked that, as the radius vector of the satellite diminishes, partial instability first supervenes from the deformation of the smaller body. It therefore hardly seems worth while to consider the partial stability of a system in which the liquid satellite (hitherto described as the smaller body) is greater than the planet. We may merely remark that in this case the problem comes to differ very little from that involved in the determination of the full secular stability of two liquid masses; for if we consider the case of a large liquid mass (the satellite) attended by a small body (the planet), it clearly makes very little difference in the result whether or not the tidal friction of the small body is included amongst the causes of instability.

This being so, I have not thought it worth while to continue the solutions of ROCHE's problem (modified by allowing the planet to be deformed) to the cases in which the satellite is larger than the planet. The ratio of the masses of satellite to planet is denoted above by λ, and the field examined by means of numerical solutions extends from $\lambda = 0$ to $\lambda = 1$, while the part omitted extends from $\lambda = 1$ to $\lambda = \infty$.

Tidal friction is a slowly acting cause of instability, and from the point of view of cosmical evolution the partial stability of ROCHE'S ellipsoids is of even greater interest than the full secular stability of the system.

The limiting stability of ROCHE'S liquid satellite is determined by the consideration that the angular momentum of the system, exclusive of the rotational momentum of the planet, shall be a minimum. This exclusion of a portion of the momentum of the whole system corresponds with the fact that we are to disregard the tidal friction of the planet as a cause of instability. If all possible cases of the liquid satellite be arranged in order of the corresponding (partial) angular momentum of the system, it is clear that for given momentum there will in general be two forms of satellite; but when the momentum is a minimum the two series coalesce. If then we proceed in order of increasing momentum, the configuration of minimum is the starting point of two series of figures; it is a figure of bifurcation, and one of the two series has one fewer degrees of instability than the other.

One of the two series is continuous with the case of a liquid satellite revolving orbitally at an infinite distance from its planet, and this is a stable configuration. Moreover, M. SCHWARZSCHILD has shown* that the whole series of ROCHE'S ellipsoids does not pass through any other form of bifurcation. Hence we conclude that of the two series which start from the configuration of minimum momentum, one is stable and the other unstable.

The unstable series of solutions is continuous with a quasi-ellipsoidal satellite, infinitely elongated along the radius vector of the orbit, and the radius vector itself is infinite. Since two portions of matter cannot occupy the same space, the infinite elongation of the satellite would be physically impossible, unless the order of infinity of the radius vector were greater than that of the longest axis of the satellite. Now it appears from the numerical results of § 25 that this is not the case, and that the satellite becomes more rapidly elongated than the radius vector increases. Hence if the solution of the problem were exact we should reach a stage at which the two masses of liquid would overlap. I shall endeavour hereafter to consider the interpretation which should be put on this result.

A series of solutions for ROCHE'S ellipsoid in limiting stability is tabulated in § 21, and the table gives the radius vector and the three semi-axes of each body. The unit of length adopted is the radius of a sphere whose volume is equal to the sum of the volumes of the two masses. Three of these solutions are illustrated in figs. 2, 3, 4. The section shown is that passing through the axis of rotation and the two centres, but the places are marked which the extremities of the mean axes would reach if the section had been taken at right angles to the axis of rotation.

The table of § 21 shows that the radius vector at which instability sets in only changes from 2·457 to 2·514, whilst λ, the ratio of the mass of the satellite to that of the planet, changes from zero to unity. The distance between the vertices of the two ellipsoids also remains wonderfully nearly constant throughout a wide range of change in the value of λ; for when $\lambda = 0{\cdot}4$ it is 0·653, and when $\lambda = 1$ it is 0·660, only falling to 0·633 at its minimum.

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* See reference in § 18 above.

Thus far I have been speaking of the modified problem of ROCHE in which the planet assumes the appropriate figure of equilibrium, but I have also obtained the solution of ROCHE's problem for an infinitely small satellite and a spherical planet. As stated in the Preface, the radius vector of limiting stability, which has been called "ROCHE's limit," is found to be 2·4553, and the axes of the critical ellipsoid are proportional to the numbers 10000, 5114, 4827. These may be compared with the 2·44 and 1000, 496, 469 determined by ROCHE himself. When we consider the methods which he employed, we must be struck with the closeness to accuracy to which he attained.

For the infinitely small satellite "the modification" of ROCHE's problem hardly introduces any sensible change in the results, but for satellites of finite mass stability will continue to subsist for a slightly smaller radius vector for the spherical than for the ellipsoidal planet. In other words, the ellipticity of the planet induces instability earlier than would be otherwise the case.

ROCHE did not attempt to investigate how closely his equations were capable of giving the ellipsoid most nearly representative of the truth, nor did he estimate how far the ellipsoid is an accurate solution. These points are considered above, and it was the desirability of making the investigation with a closer degree of accuracy which occasioned many of the difficulties encountered.

For the infinitely small satellite the ellipsoidal solution is exact, and with a spherical planet, but not for an ellipsoidal one, ROCHE's equations give that ellipsoid exactly. In this case, however, the change introduced by the modification of ROCHE's problem is quite unimportant.

For finite satellites ROCHE's equations require sensible modification, and the solution of the "modified" problem is different from that of the unmodified one, although not to an important extent. But the ellipsoid derived from the corrected equations is deformed by an infinite series of ellipsoidal harmonic deformations, beginning with terms of the third order. Of these, the only ones which have any sensible effect are those which may be described as zonal with respect to the satellite's radius vector.

By far the most important of these is the third zonal harmonic, whereby the satellite assumes a somewhat pear-shaped figure, being sharpened towards the stalk end of the pear pointing towards the planet, and bluntened at the other end. In consequence of this deformation the shape is slightly flattened between the stalk and the middle.

The fifth and successive odd zonal harmonics accentuate the sharpening of the stalk and the bluntening of the remote end. The fourth, sixth, and successive even harmonics also accentuate the protrusion of the stalk, but tend to fill up the deficiency at the remote end.

The general effect must be very like what results from the second approximation to the pear-shaped figure of equilibrium,[*] for I found that the ellipsoidal form was but slightly changed over the greater part of the periphery, whilst a protrusion occurred at one end—in this present case pointing towards the planet.

In figs. 2, 3, 4, the protrusions at one end and the bluntening at the other, as computed from the third, fourth, and fifth harmonics, are indicated by dotted lines. It appears from these figures that, at least up to the point when instability sets in, the ellipsoid remains surprisingly near to the correct solution.

For an infinitely small satellite minimum radius vector also gives minimum angular momentum, so that the closest possible satellite is also in a state of limiting stability. But this is not the case for finite satellites, and there exists an unstable ellipsoidal satellite with smaller radius vector than is consistent with stability. Thus for a satellite of four-fifths of the mass of the planet the minimum radius vector is 2·36, whilst stability ceases at a distance of 2·50. Again, for equal masses stability ceases at 2·514, whilst the possibility of an ellipsoidal solution extends to 2·343.

If we follow the forms of the more and more elongated satellites, when the radius vector has begun to increase again, we find explicitly in the case of equal masses, and with practical certainty for all ratios of masses, that the distance between the two vertices continues to diminish and finally becomes negative. At this stage the two masses overlap, a conclusion which is, of course, physically impossible. But the calculation is based on the assumed adequacy of the approximations, and it is certain that the harmonic deformations of the ellipsoids increase rapidly, so that each body puts out a protrusion towards the other. The two masses of liquid must therefore really meet before we reach the stage of overlapping ellipsoids. As far as can be seen, the approximation has become very imperfect—perhaps evanescent—before the two ellipsoids cross. It will be best to continue the discussion of the meaning of this result after we have considered the true secular stability of the two masses of liquid.

If a satellite, being a particle, revolves about a rotating planet, whose tides are subject to friction, there are, for given angular momentum, two configurations (if any) in which the planet always presents the same face to the satellite. In one of these, which is unstable, the satellite is close to the planet; in the other, which is stable, it is remote.[†] If the angular momentum of the system be diminished, the radius vector of the stable configuration diminishes and that of the unstable one increases until the two coalesce. For yet smaller angular momentum there is no configuration possible in which the planet shall always present the same face to the satellite. We see then that amongst all possible configurations in which the planet presents the same face to the satellite, that one is in limiting stability, in which the two solutions coalesce with minimum angular momentum.

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[*] See 'Stability,' referred to in the Preface.

[†] See 'Roy. Soc. Proc.,' No. 197, 1879, or Appendix G (*b*) to vol. II. of THOMSON and TAIT's 'Natural Philosophy.'

A rotating liquid planet will continue to repel its satellite so long as it has any rotational momentum to transfer to the orbital momentum of the satellite. Hence an infinitesimal satellite will be repelled to infinity, and the configuration of limiting stability for an infinitesimal satellite attending a planet, which always presents the same face to it, is one with infinite radius vector.

Very nearly the same conditions hold good when both planet and satellite are subject to frictional tides. In § 2 it is proved that when each body is constrainedly spherical, the radius vector of limiting stability is infinite when the ratio of the masses is infinitely small. The radius vector decreases with great rapidity as the ratio of the masses increases, and when the masses are equal, the radius vector of limiting stability is 1·738 times the radius of a sphere whose mass is equal to the sum of the masses, or is 2·19 times the radius of either of the two spheres. Thus, when the ratio of the masses falls from zero to unity (and this embraces all possible cases), limiting stability occurs with a radius vector which falls from infinity until the two spheres are only just clear of one another.

When we pass from the case of the two spheres to that of two masses, each of which is a figure of equilibrium under the attraction of itself and its companion, and subject to centrifugal force, the calculation becomes exceedingly complicated. Since the radius vector of limiting stability in every case must be greater than that of ROCHE's ellipsoid in limiting stability, and since in the latter case instability sets in through the deformation of the smaller body, it follows that in every case of true limiting secular stability of the system, instability supervenes through tidal friction.

When the ratio of the masses is small, we have seen that limiting stability occurs when the two masses are far apart. In this case the deformations of figure are small, and could easily be computed by spherical harmonic analysis.

For finite values of the ratio of masses, when spherical harmonic analysis would fail, a fair degree of exactness in the result may be obtained from the approximate formula of § 19. There would be no serious error from this formula when the ratio of masses is less than a half, but for greater values of the ratio it seems necessary to have recourse to the laborious processes employed in determining ROCHE's ellipsoids. I thought, then, that it might suffice to compute the configuration of true secular limiting stability in the case of equal masses. It is illustrated in fig. 5, and we see that the radius vector is 2·638. We found that for a pair of equal spheres, instability only set in when the radius vector, measured in the same unit, was 1·738. Thus the deformations of the two masses forbid them to approach as near to one another as if they were spheres. It should be noted that instability in this case must arise from tidal friction, because ROCHE's ellipsoid in limiting stability was found to have a radius vector of 2·514.

When POINCARÉ announced that there is a figure of equilibrium bearing some resemblance to a pear, he also conjectured that the constriction between the stalk and the middle of the pear might become developed until it became a thin neck of liquid joining two bulbs, and that yet further the neck might break and the two masses become detached. References to my own papers on this pear-shaped figure and its stability are given above in the preface, and the present investigation was undertaken in the hope that a revision of ROCHE's work would throw some light on the figure when the constriction has developed into a thin neck of liquid.

As a preliminary to greater exactness, I have in § 3 considered the motion of two masses of liquid, each constrainedly spherical, and joined to one another by a weightless pipe. Through such a pipe liquid can pass from one sphere to the other, and it will continue to do so until, for given radius vector, the spheres bear some definite ratio to one another; or, to state the matter otherwise, two spherical masses of given ratio, revolving in a circular orbit without relative motion, can be started with some definite radius vector so that liquid will not flow from one to the other.

In this system the ratio of the masses and the radius vector are the only parameters, and I find that the condition of equilibrium is a cubic equation in the radius vector with coefficients which are functions of the ratio of the masses. The cubic has three real roots of which only one has a physical meaning, and the solution is illustrated graphically in fig. 1. The single circle on the right is the larger sphere, and it is maintained of constant size for convenience of illustration. The smaller circles on the left represent the solutions for various ratios of masses, which are the cubes of the numbers written on the successive circles.

The solution of this problem seems to me very curious, but it does not possess much physical interest, since it is proved in § 3 that all the solutions are unstable.

The distance between the two masses is much smaller than is the case with any of ROCHE's ellipsoids, even with minimum radius vector, and accordingly it did not seem probable that the parallel problem, when the two masses are liquid and deformed, would possess any solution at all; nevertheless, it was worth while to pursue the investigation to the end.

When the masses are ellipsoidal and are joined by a weightless pipe, the solution would become very complicated, but the question may be attacked indirectly. When the masses are spherical there is a certain function of the radius vector and of the ratio of the masses which must vanish when a channel of communication is opened between them. If this function be computed for two given spherical masses with given radius vector, we find that it is negative if the two masses are too close together to admit of junction by a pipe without disturbance of their relative masses, and that it is positive if they are too far apart.

When the figures of equilibrium of two detached masses of liquid are determined, it is possible to form the corresponding function, but part of it consists of an infinite series of which it is only practically possible to give the first few terms. Now I have computed this function in a number of cases of ROCHE's ellipsoids, and have found that the few terms of the infinite series are small, that the series is apparently rapidly convergent, and that the function is decisively positive. We may conclude then that in none of the cases, for which numerical results have been given, is it even approximately possible to make a junction between the masses; and even if we could do so, the system would be unstable, because removal of a constraint may destroy but cannot impart stability. To find any possible solution we must consider cases where the two masses are much closer together.

I think, however, that there must be a figure of the kind sought, for the following reasons: If the function referred to above be formed for given radius vector and ratio of masses, we find that its value is very much less than if the two masses are spherical. Thus the tendency of liquid to flow from the larger to the smaller mass (when they are too far apart) is much less than if the two masses were spherical. Every increase of ellipticity in the ellipsoids tends to diminish the function, and the series tends to become less convergent; and besides I have made no attempt to evaluate the terms in the function which correspond to the harmonic inequalities of the ellipsoids, and these would tend to diminish the function still further.

It was remarked above that two much elongated ellipsoids seem to coalesce finally, but that the approximations were not satisfactory. I find, however, that even to the end the function, as far as it could be computed, was still positive although much diminished. It appears to me then probable that if we could obtain a more complete expression for the function, we should find that it vanishes before the two ellipsoids overlap. There is then some reason to believe in the existence of a figure of equilibrium consisting of two quasi-ellipsoids joined by a narrow neck; but such a figure must be unstable.

I have, in fig. 6, made a highly conjectural drawing of such a figure where the two bulbs are equal. The data are derived from the computations for the much elongated ellipsoids just before they are found to overlap.

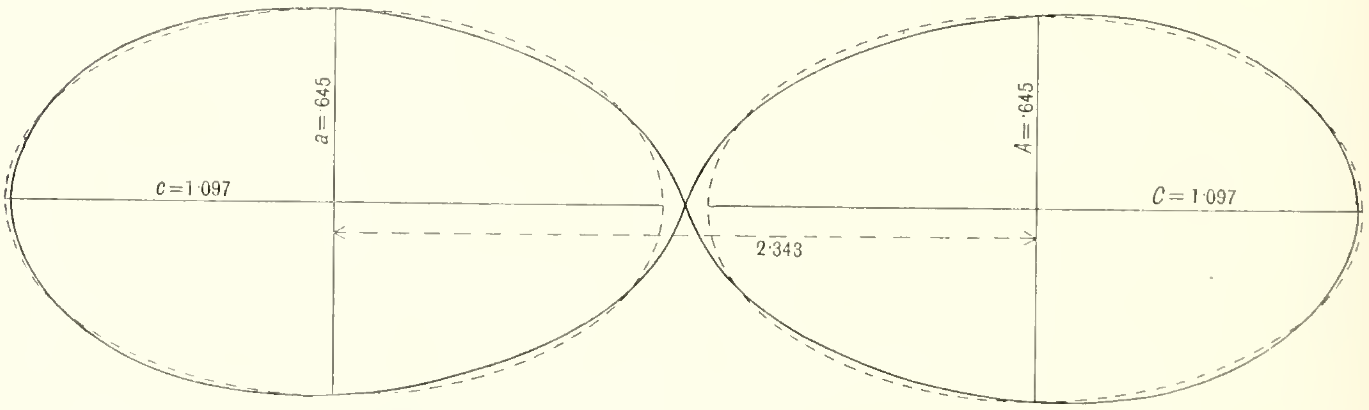

Fig. 6. Conjectural drawing of unstable figure of two equal masses of liquid just in contact.

Mr. Jeans has considered the equilibrium and stability of infinite rotating cylinders of liquid. This is the two-dimensional analogue of the three-dimensional problem.* He finds solutions perfectly analogous to MACLAURIN'S and JACOBI'S ellipsoids and to the pear-shaped figure. In consequence of the greater simplicity of the conditions, he is able to follow the development of the cylinder of pear-shaped section until the neck joining the two parts has become quite thin. His analysis, besides, points to the rupture of the neck, although the method fails to afford the actual shapes and dimensions in this last stage of development.

He is able to prove conclusively that the cylinder of pear-shaped section is stable, and it is important in connection with our present investigation to note that he finds no evidence of any break in the stability of that cylinder up to its division into two parts.

The stability of MACLAURIN'S and of the shorter Jacobian ellipsoids is, of course, well established, and I imagined that the pear-shaped figure with incipient furrowing was also proved to be stable. But M. LIAPOUNOFF now states† that he is able to prove the pear-shaped figure to be unstable from the beginning, and he attributes the discrepancy between our conclusions to the fact that my result depended on the supposed rapid convergency of an infinite series, of which only a few terms were computed. The terms computed diminish rapidly, and it seemed to me evident that the rapid diminution must continue, so that I feel unable to accept the hypothesis that the sum of the neglected terms could possibly amount to the very considerable total which would be necessary to reverse my conclusion. I am, therefore, still of opinion that the pear-shaped figure is stable at the beginning; and this view receives a powerful confirmation from Mr. JEANS'S researches. The final decision must await the publication of M. LIAPOUNOFF'S investigation.

But there is another difficulty raised by the present paper. I had fully expected to find an approximation to a stable figure consisting of two bulbs joined by a thin neck, but while my work indicates the existence of such a figure, it seems to me, at present, conclusive against its stability. The weightless pipe joining two bulbs of fluid is clearly only a crude representative of a neck of fluid, but I find it hard to imagine that it is so very imperfect that the reality should be stable, while the representation is unstable. My present investigation shows that two quasi-ellipsoids just detached from one another do not possess secular stability. The vertices of such bodies would be blunt points nearly in contact; the introduction of a short pipe without weight between these blunt points would differ exceedingly little from two sharp points actually in contact. Is it possible that the difference would produce all the change from great instability even to limiting stability? The opening of a channel between the two masses is the removal of a constraint; the system does not possess true secular stability when the channel is closed, and we should have to believe that the removal of a constraint induces stability; and this is, I think, impossible.

If, then, Mr. JEANS is right in believing in the stable transition from the single cylinder to two revolving about one another, and if I am correct now, the two problems must part company at some undetermined stage. M. LIAPOUNOFF will no doubt contend that it is at the beginning of the pear-shaped series, but for the present I should disagree with such an opinion.

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* "On the Equilibrium of Rotating Liquid Cylinders," 'Phil. Trans.,' A, vol. 200, pp. 67–104.

† See reference in Preface.

I have no suggestion to make as to the stage at which the pear-shaped figure may become unstable, or as to the figure which must be coalescent with it when instability supervenes. These points must await the elucidation which they will no doubt receive from future investigations.

One question remains: If my present conclusions are correct, do they entirely destroy the applicability of this group of ideas to the explanation of the birth of satellites or of double stars? I think not, for we see how a tendency to fission arises, and it is not impossible that a period of turbulence may naturally supervene in the process of separation. Finally, as Mr. JEANS points out, heterogeneity of density introduces new and important differences in the conditions.

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THE ASYMPTOTIC EXPANSION OF INTEGRAL FUNCTIONS DEFINED BY TAYLOR'S SERIES

BY

E. W. BARNES, M.A.,
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NATURAL HISTORY

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By E. W. BARNES, *M.A., Fellow of Trinity College, Cambridge.*

Communicated by Professor A. R. FORSYTH, *Sc.D., LL.D., F.R.S.*

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INTRODUCTION.

§ 1. Integral functions can be defined either by TAYLOR'S series or Weierstrassian products. When the zeros are simple functions of their order number, the latter method is, as a rule, most simple. When the zeros, however, are transcendental functions of the order number, those integral functions which so far have occurred in analysis have been defined by TAYLOR'S series.

[Definitions by definite integrals have usually been reducible to one of the preceding forms.]

Whatever be the manner of its definition, an integral function has a single essential singularity at infinity, and the behaviour near this singularity serves to classify the function. By studying this behaviour we may hope to find connecting links between the two modes of definition.

The behaviour at infinity is determined by asymptotic expansions.

The first expansion of a function was derived from STIRLING'S[1] approximation to n!. This led naturally to expressions for $\Gamma(x)$ when x is large and real.

---

[1] STIRLING, 'Methodus Differentialis,' 1730.

Such were considered by, among others, CAUCHY,[1] BINET,[2] and RAABE.[3] Other references to the history of the subject will be found in the "Encyklopädie der Mathematischen Wissenschaften."[4]

But the behaviour of a function defined by a Weierstrassian product, when considered only for real values of the variable near infinity, affords little knowledge of the essential singularity. STIELTJES[5] first proved the asymptotic expansion for $\Gamma(x)$ to be valid for all values of $|\arg x| < \pi$. His result was subsequently obtained by MELLIN.[6] Immediately afterwards the author,[7] from an idea suggested by one of MELLIN'S earlier papers and due originally to RIEMANN,[8] extended the result to the multiple gamma functions. Then, simultaneously, MELLIN[9] and the author[10] discovered the asymptotic expansions for large classes of integral functions defined by Weierstrassian products. Such investigations have been developed by the author in a series of papers.[11]

It is natural to expect that similar results can be obtained for functions defined by TAYLOR'S series.

An asymptotic expansion for BESSEL'S function $J_0(x)$ was first given for real values of x by POISSON.[12] The result was extended to other integral values of n, that is to say, to functions $J_n(x)$, where n is an integer, by JACOBI.[13] Then, in a noteworthy paper, HANKEL[14] extended the result to general complex values both of the parameter n and the variable x; and though his statement of his results merited the criticism of HURWITZ,[15] it deserves recognition as a valuable discovery. The question has since been considered, among others, by WEBER[16] and NIELSEN[17]. Further references will be found in the 'Encyklopädie'[18] and in NIELSEN'S text book.[17]

In this connection mention may be made of a similar investigation by HOBSON[19] in the theory of LEGENDRE'S functions.

Closely allied to BESSEL'S function are integral functions defined by generalised hypergeometric functions. Here for real values of the variable STOKES[1] first gave asymptotic expansions, and ORR[2] has recently extended his results to general complex values of the argument.

---

[1] CAUCHY, 'Exercices d'Analyse,' tome 2, p. 386.

[2] BINET, 'Journal de l'École Polytechnique,' tome 27, p. 220.

[3] RAABE, 'Crelle,' vol. 25, p. 147; vol. 28, p. 10.

[4] BRUNEL, *loc. cit.*, vol. 2, A, p. 166.

[5] STIELTJES, 'Liouville,' sér. 4, vol. 5, p. 425.

[6] MELLIN, 'Acta Societatis Scientiarum Fennicae,' tome 24, No. 10.

[7] BARNES, 'Phil. Trans. Roy. Soc.,' A, vol. 196, p. 265.

[8] RIEMANN, 'Œuvres,' 1898, p. 165.

[9] MELLIN, 'Acta Societatis Scientiarum Fennicae,' tome 29, No. 4.

[10] BARNES, 'Phil. Trans. Roy. Soc.,' A, vol. 199, pp. 411–500.

[11] BARNES, 'Cambridge Phil. Trans.,' vol. 19, pp. 322–355; pp. 426–429; 'Proc. Lond. Math. Soc., ser. 2, vol. 3, pp. 253–272, and pp. 273–295.

[12] POISSON, 'Journal de l'École Polytechnique,' tome 19, p. 349.

[13] JACOBI, 'Gesammelte Werke,' vol. 7, p. 174.

[14] HANKEL, 'Mathematische Annalen,' vol. 1, pp. 467–501.

[One of the referees has pointed out that I had omitted to mention the brilliant investigation of STOKES, which remained long unknown to continental mathematicians. STOKES obtained the asymptotic expansions of the solutions of BESSEL'S equation for complex values of the variable in two papers published in 1857 and 1868 respectively ('Cambridge Philosophical Transactions,' vol. 10, p. 105; vol. 11, p. 412). The reader may also notice STOKES' 'Cambridge Philosophical Proceedings,' vol. 6, p. 362, and 'Acta Mathematica,' vol. 26, pp. 393–397.]

[15] HURWITZ, 'Mathematische Annalen,' vol. 33, p. 246.

[16] WEBER, 'Mathematische Annalen,' vol. 6, p. 148.

[17] NIELSEN, 'Handbuch der Cylinderfunctionen,' 1904, pp. 156, &c.

[18] WANGERIN, 'Encyklopädie der Mathematischen Wissenschaften,' Band 2, A, p. 748.

[19] HOBSON, 'Phil. Trans.,' A, vol. 187, pp. 443–531.

Quite recently MITTAG-LEFFLER[3] has constructed the new function $E_\alpha(x)$ and investigated its asymptotic behaviour.

It was, however, in the theory of linear differential equations that POINCARÉ[4] first pointed out the use of divergent series as solutions in the neighbourhood of infinity, and laid the foundation of a rigorous theory of such series. The continuation of his investigations has been the subject of many researches, notably by KNESER and HORN. For references in this connection I may refer the reader to FORSYTH'S 'Theory of Differential Equations.'[5]

Another connected series of investigations may be mentioned. HADAMARD[6] first gave a remarkable theorem as to the maximum value of the modulus of an integral function defined by TAYLOR'S series on a circle of large radius. Other theorems of similar type are due to BOREL[7] and BOUTROUX.[8] Valuable, however, as such theorems are on account of their generality, we need complete asymptotic expansions before we can adequately classify integral functions. Further references will be found in BOREL'S[9] text-book.

There is a close connection between the asymptotic expansions of certain types of integral functions and what BOREL[10] has called the associated functions defined by TAYLOR'S series of finite radius of convergence. This connection enables us to investigate the singularities of many types of such TAYLOR'S series, and thus connects the theory with a whole series of investigations. Reference may be made to the work of FABRY,[11] LE ROY,[12] LINDELÖF,[13] and LEAU.[14] A very complete bibliography of this branch of modern mathematics is given by HADAMARD.[15]

§ 2. In the present paper the author attempts to give unity to the investigations of asymptotic expansions of integral functions defined by TAYLOR'S series by taking various standard types of such functions and applying new methods of contour integration so as to get, as simply and elegantly as possible, complete asymptotic expansions. For each function investigated we find the nature of the behaviour at infinity. The investigation may be regarded as preliminary to the formation of a classified table: it is complementary to that previously carried out for functions defined as products.

It is hardly necessary, perhaps, to say that no methods, however powerful, will apply to every function that can be constructed by a TAYLOR'S series. Just as, in general, a TAYLOR'S series admits its circle of convergence as a line of essential singularity, so the general integral function, which we may define by a TAYLOR'S series, will not admit the same dominant asymptotic expansion for any range of values of arg x, however small.

---

[1] STOKES, 'Cambridge Phil. Soc. Proc.,' vol. 6, pp. 362–366.

[2] ORR, 'Cambridge Phil. Soc. Trans.,' vol. 17, pp. 171–200; pp. 283–290.

[3] MITTAG-LEFFLER, 'Comptes Rendus,' vol. 137, pp. 554–558; 'Acta Mathematica,' vol. 29.

[4] POINCARÉ, 'Acta Mathematica,' tome 8, pp. 295–344.

[5] FORSYTH, *loc. cit.*, Part III., vol. 4, 1902, p. 341.

[6] HADAMARD, 'Liouville,' sér. 4, vol. 9, pp. 171–215.

[7] BOREL, 'Acta Mathematica,' vol. 20, pp. 357–396.

[8] BOUTROUX, 'Acta Mathematica,' vol. 28, pp. 1–128.

[9] BOREL, 'Leçons sur les Fonctions Entières,' 1900.

[10] In the memoir just cited.

[11] FABRY, 'Annales de l'École Normale Supérieure,' sér. 3, tome 13, pp. 367–399; 'Acta Mathematica,' tome 22, pp. 65–87; 'Liouville,' sér. 5, tome 4, pp. 317–358.

[12] LE ROY, 'Annales de la Faculté des Sciences de Toulouse,' sér. 2, tome 2 (1900).

[13] LINDELÖF, 'Acta Societatis Scientiarum Fennicae,' tome 24, No. 7.

[14] LEAU, 'Liouville,' sér. 5, tome 5, pp. 365–425.

[15] HADAMARD, "La Série de Taylor et son prolongement analytique" ('Scientia,' 1901).

In conclusion, I must mention a paper of HARDY[1] in which he obtains some of the present results. He was led to the question of asymptotic behaviour by a desire to obtain approximations for the large zeros of integral functions, one of the subsidiary problems which a general knowledge of integral functions will solve. His paper was sent to me in August, 1904, in the capacity of referee to the London Mathematical Society. He had obtained the first terms of the asymptotic forms of the function which I call $G_\beta(x;\theta)$ in the case where β and θ are real. In my reply I said that I had already obtained complete expansions for general complex values of β and θ. Such results Mr. HARDY has since published in the revised form of his paper. The reader will find it instructive to compare our respective discussions of the question.

[*Note added March* 21, 1906.—The Council of the Royal Society suggested that the paper in its original form contained so many developments that it was more of the nature of a treatise than of a paper to be published in their Transactions. In consequence it has been considerably compressed, and statements of results have been in many cases given in lieu of detailed investigations. Developments of such a nature will, I hope, with my subsidiary investigations, be suitable for publication elsewhere. In compressing the paper, certain changes have at times been made in the mode of presentation. Whenever such a change has been made, or whenever a result has been stated which had not been originally obtained, the number of the corresponding paragraph is placed in square brackets [ ].]

Preliminary Definitions and Theorems.

§ 3. The function $f(x)$ is said to admit the asymptotic expansion

$$c_0 + \frac{c_1}{x} + \frac{c_2}{x^2} + \ldots$$

for a given range of values of arg x, when $|x|$ is large, if the following condition is satisfied. We put

$$\left| f(x) - c_0 - \frac{c_1}{x} - \ldots - \frac{c_n}{x^n} \right| = R_n.$$

Then it must be possible, for any assigned value of n, to find a value X for $|x|$ such that, whenever

$$|x| > X, \quad |x^n R_n| < \epsilon,$$

where ϵ is any arbitrarily assigned small positive quantity.

The solution of linear differential equations often gives rise to series of which the simplest type is

$$e^x \left[c_0 + \frac{c_1}{x} + \ldots + \frac{c_n}{x^n} + \ldots \right],$$

the series within the brackets being divergent.

We say that $f(x)$ is asymptotically represented by such a series for any value or range of values of arg x under the following conditions.

Put

$$\left| f(x) - e^x \left[c_0 + \frac{c_1}{x} + \ldots + \frac{c_n}{x^n} \right] \right| = R_n.$$

---

[1] HARDY, "On the Zeros of Certain Classes of TAYLOR'S Series," Part II., 'Proc. Lond Math. Soc.,' ser. 2, vol 2, pp. 401–431.

Then for any assigned value of n it is possible to find a value X for $|x|$ such that, whenever $|x| > X$,

$$|e^{-x}x^n R_n| < \epsilon,$$

where ϵ is an arbitrarily assigned positive quantity.

It is evidently possible that an asymptotic expansion may hold for some values of arg x and not for others.

§ 4. The following definitions give precision to subsequent statements.

When we say of a quantity $J(x, k)$ that, for any assigned value or range of values of arg x, it is of order less than $1/|x|^k$ when $|x|$ is large, we mean that for any assigned value of k it is possible to find a value X of x such that, when $|x| > X$,

$$|J(x, k)\, x^k| < \epsilon,$$

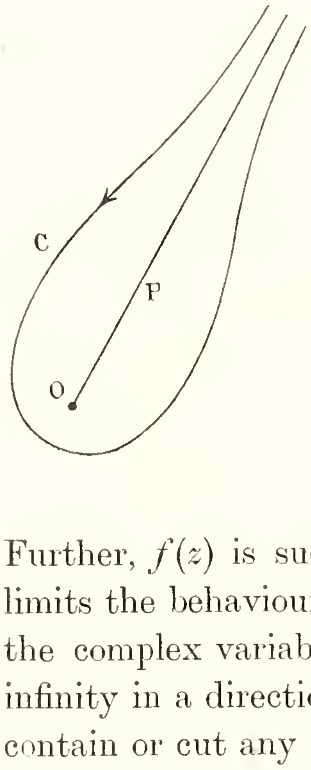
ϵ being defined as before.

When we say that $J(x, k)$ tends exponentially to zero with $1/|x|$, we mean that it is such that, when $|x| > X$ and $\mathfrak{R}(x) > 0$,

$$|J(x, k)\, e^{px}| < \epsilon,$$

p being a definite finite positive quantity.

§ 5. Our fundamental procedure is based upon the following theorem.



Suppose that, when $|x|$ is large, we wish to find an asymptotic expansion for the integral

$$I = \frac{\iota}{2\pi}\int_C e^{-xz} f(z)\,(-z)^{\beta-1}\,dz.$$

The integral is taken round a gamma-function contour C which encloses the origin and embraces an axis P from the origin to infinity along which $\mathfrak{R}(xz)$ is positive.

In the subject of integration $f(z)$ is a function which, for values of $|z| < l$, admits the convergent expansion

$$f(z) = \sum_{n=0}^{\infty} c_n (-z)^n.$$

Further, $f(z)$ is such that the integral I is convergent. This condition, of course, limits the behaviour of $f(z)$ at infinity along the axis P. Suppose that the plane of the complex variable z is dissected by lines passing away from the poles of $f(z)$ to infinity in a direction away from the origin. We assume that the contour C does not contain or cut any of these lines.

Then the integral I admits the asymptotic expansion

$$\sum_{n=0}^{\infty} c_n \frac{\iota}{2\pi}\int_C e^{-xz}(-z)^{\beta+n-1}\,dz = \sum_{n=0}^{\infty} \frac{c_n}{\Gamma(1-\beta-n)\,x^{\beta+n}}.$$

Divide up the contour C into two parts L and M. L lies wholly within the circle of convergence of $f(z)$ and, on L, $|z| \eqslantless l'$, where $l' = l - \epsilon$ and ϵ is a positive quantity as small as we please. M forms the remainder of the contour.

We have

$$\mathrm{I} - \sum_{n=0}^{k-1} \frac{c_n}{\Gamma(1-\beta-n)\, x^{\beta+n}} = \frac{\iota}{2\pi} \int_{\mathrm{C}} e^{-xz} \left\{ f(z) - \sum_{n=0}^{k-1} c_n (-z)^n \right\} (-z)^{\beta-1}\, dz$$

$= \mathrm{I}_1 + \mathrm{I}_2$ (say), where I_1 is the integral taken along the contour L and I_2 the sum of the integrals along the two parts of the contour M.

In the first integral I_1 put $xz = \zeta$ and let L′ be the transformed contour. The integral becomes

$$\frac{\iota}{x^{\beta+k} 2\pi} \int_{\mathrm{L}'} e^{-\zeta} \left[\left(-\frac{x}{\zeta}\right)^k \sum_{n=k}^{\infty} c_n \left(-\frac{\zeta}{x}\right)^n \right] (-\zeta)^{k+\beta-1}\, d\zeta.$$

For any assigned finite value of k, however large,

$$\left| \left(-\frac{x}{\zeta}\right)^k \sum_{n=k}^{\infty} c_n \left(-\frac{\zeta}{x}\right)^n \right| = \left| c_k - c_{k+1} \frac{\zeta}{x} + c_{k+2} \left(\frac{\zeta}{x}\right)^2 - \dots \right|$$
$$< |c_k| + |c_{k+1}|\, l' + |c_{k+2}|\, l'^2 + \dots$$

This series is absolutely convergent and independent of x or ζ. We may therefore say that

$$\left| \left(-\frac{x}{\zeta}\right)^k \sum_{n=k}^{\infty} c_n \left(-\frac{\zeta}{x}\right)^n \right| < \mathrm{R}_k,$$

where R_k is independent of x or ζ, and is finite when k is finite.

Hence

$$|\mathrm{I}_1| < \frac{1}{|x^{\beta+k}|} \left| \frac{\iota}{2\pi} \right| \left| \int_{\mathrm{L}'} |e^{-\zeta}|\, \mathrm{R}_k\, |(-\zeta)^{k+\beta-1}|\, |d\zeta| \right|.$$

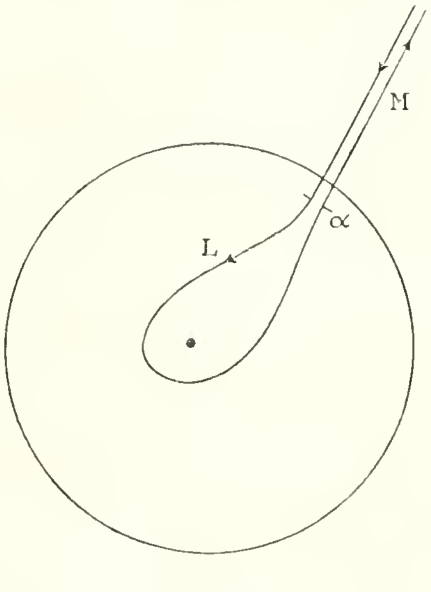
Thus $|x^{\beta+k-1} \mathrm{I}_1|$ can be made as small as we please by taking $|x|$ sufficiently large.

Consider in the next place the integral I_2.

If the original contour cut none of the lines of dissection of the plane, it may be closed up as in the figure. For, as we pass over no poles of the subject of integration, by CAUCHY's theorem we do not alter its value. The contour integral I_2 can therefore be replaced by

$$\frac{\sin \pi\beta}{\pi} \int e^{-xz} z^{\beta-1} \left[f(z) - \sum_{n=0}^{k-1} c_n (-z)^n \right] dz,$$

a line integral taken from the point α along the axis P to infinity.



If we put $z = \alpha + \zeta/x$, we get

$$\mathrm{I}_2 = \frac{\sin \pi\beta}{\pi} e^{-\alpha x} \int_0^{\infty} e^{-\zeta} (\alpha + \zeta/x)^{\beta-1} \left[f(\alpha + \zeta/x) - \sum_{n=0}^{k-1} c_n (-\alpha - \zeta/x)^n \right] d\zeta/x,$$

and the integral is taken along a line for which $\mathfrak{R}(\zeta)$ is positive.

By our original hypothesis the integral is convergent. It is finite for any assigned finite value of k, and when $|x|$ is very large it tends to a finite limit.

Hence $|\mathrm{I}_2|$ tends exponentially to zero with $1/|x|$.

Therefore for all finite values of k however large we may take $|x|$ so large that

$$\left| \mathrm{I} - \sum_{n=0}^{k-1} c_n/x^{\beta+n}\Gamma(1-\beta-n) \right| \, |x^{\beta+k-1}|$$

tends to zero as $|x|$ increases.

Therefore I admits the asymptotic expansion

$$\sum_{=0}^{\infty} c_n/x^{\beta+n}\Gamma(1-\beta-n).$$

Inasmuch as $f(z)$ admits $\sum_{n=0}^{\infty} c_n z^n$ as a summable divergent series on the dissected plane, we may say that, for our process for deriving an asymptotic expansion from an integral of the specified type to be possible, the contour C must be such that for all points on and within it $f(z)$ must be representable by the summable divergent series.

PART I.

The Function $\mathrm{G}(x\,;\theta) = \sum_{n=0}^{\infty} \dfrac{x^n}{\Gamma(n+1)(n+\theta)}$.

§ 6. The function $\mathrm{G}(x\,;\theta)$ is a particular case of the function $\mathrm{G}_\beta(x\,;\theta)$ which will be considered in Part III. It can be discussed by more simple methods than are used in the more general case, and some of the formulæ can only be deduced from the latter by employing the calculus of limits. I give here a brief summary of results and refer the reader elsewhere* for detailed analysis. We assume that θ is not zero or a negative integer.

I. By considering the contour integral

$$-\frac{1}{2\pi\iota}\int \frac{\Gamma(-s)\,x^s}{s+\theta}\,ds$$

we can prove that

$$\mathrm{G}(-x\,;\theta) = -e^{-x}\sum_{n=0}^{k} \frac{(\theta-1)\ldots(\theta-n)}{x^{n+1}} + \frac{(\theta-1)\ldots(\theta-k-1)}{x^{k+1}}\,\mathrm{G}(-x\,;\theta-k-1).$$

II. If $|\arg x| < \pi$,

$$\mathrm{G}(-x\,;\theta) - x^{-\theta}\Gamma(\theta) = -x^{-\theta}\int_x^{\infty} e^{-y}y^{\theta-1}\,dy,$$

where the line of integration is straight, tends to infinity in the positive half of the y-plane, does not cut the negative half of the real axis, and avoids the origin.

---

* See the 'Quarterly Journal of Mathematics,' 1906, vol. 37, pp. 289–313.

III. If $|\arg x| < \pi$, we have the asymptotic expansion

$$G(-x;\theta) = \Gamma(\theta)\,x^{-\theta} - e^{-x}\sum_{n=0}^{\infty}\frac{(\theta-1)\ldots(\theta-n)}{x^{n+1}}.$$

When $|\arg x|$ is very small, we have the asymptotic expansion

$$G(x;\theta) = e^{x}\sum_{n=0}^{\infty}\frac{(1-\theta)\ldots(n-\theta)}{x^{n+1}}.$$

These expansions are truly asymptotic in the sense of § 3.

IV. The large zeros of $G(x;\theta)$ occur near the positive or negative directions of the imaginary axis.

PART II.

The Function $g(x;\theta)$ defined, when $|x|<1$, by the TAYLOR'S *series* $\sum_{n=0}^{\infty}\frac{x^n}{n+\theta}$.

§ 7. This function is, in BOREL'S language, the function associated with $G(x;\theta)$. It is a particular case of the more general function considered in Part IV. The detailed analysis is given in the paper to which reference was made in Part I.

I. The function $g(x;\theta)$ can, for all values of x except those which lie on the real axis between 1 and $+\infty$ (the limits included), be represented by the system of integrals

$$\frac{1}{2\pi\iota}\int_{D} G(xz;\theta)\log(-z)\,e^{-z}dz,$$

where D is a contour which encloses the origin and embraces some line in the positive half of the z-plane along which the integral is finite, and where $\log(-z)$ is real when z is real and negative and has a cross cut along this line.

II. We deduce that the only finite singularities of $g(x;\theta)$ must lie on the real axis between $x = 1$ and $x = +\infty$ (the limits included).

III. By using I., coupled with the asymptotic expansion of $G(x;\theta)$, we can show that, if $|\arg x| < \pi/2$, and $|(1-x)/x| < 1$,

$$-g(x;\theta)-\psi(\theta)\,x^{-\theta} = \sum_{n=0}^{\infty}\frac{(\theta-1)\ldots(\theta-n)}{n\,!}\frac{(1-x)^n}{x^{n+1}}\{\log(1-x)-\psi(n+1)\}.$$

This formula gives the nature of the singularity of $g(x;\theta)$ at $x = 1$, and shows that $g(x;\theta)$ has no other singularities in the finite part of the plane.

IV. The function $xg(x;\theta)+x^{1-\theta}\log(1-x)$ satisfies the differential equation

$$x\frac{d\eta}{dx}+(\theta-1)\,\eta = x\,\frac{1-x^{1-\theta}}{1-x}.$$

By considering this equation we may again deduce the expansion, valid when $\mathfrak{R}(x) > \frac{1}{2}$,

$$g(x;\theta) + x^{-\theta}\log(1-x) = \{\psi(1) - \psi(\theta)\}x^{-\theta}$$
$$+ \sum_{n=1}^{\infty} \frac{(1-x)^n}{x^{n+1}} \frac{(\theta-1)\ldots(\theta-n)}{n!}\left(\frac{1}{1} + \ldots + \frac{1}{n}\right).$$

V. We may equally show that, when $|1-x|$ is sufficiently small,

$$x^{\theta} g(x;\theta) + \log(1-x) = \psi(1) - \psi(\theta) + \log x - \sum_{n=1}^{\infty} S_{n-1}(\theta)(\log x)^n/n!,$$

where $S_{n-1}(\theta)$ is the $(n-1)^{\text{th}}$ simple Bernoullian function of θ of parameter unity.

VI. When θ is not a positive or negative integer or zero, we have, if $|x| > 1$, and $|\arg(-x)| < \pi$,

$$g(x;\theta) = -\sum_{n=1}^{\infty} \frac{1}{x^n(\theta-n)} - (-x)^{-\theta}\frac{\pi}{\sin \pi\theta}.$$

This formula gives the asymptotic value of $g(x;\theta)$ when $|x|$ is very large.

PART III.

The Function $G_{\beta}(x;\theta) = \sum_{n=0}^{\infty} \frac{x^n}{n!(n+\theta)^{\beta}}$.

§ 8. This function is the generalisation of that considered in Part I. We assume that θ is not zero or a negative integer, and further that

$$(n+\theta)^{\beta} = \exp\{\beta \log(n+\theta)\},$$

wherein the absolute value of the imaginary part of $\log(n+\theta)$ is less than π.

If θ be real and negative, this convention fails to define $(n+\theta)^{\beta}$ for those terms for which $(n+\theta) < 0$. In these cases we may assume that the imaginary part of $\log(n+\theta)$ is equal to $+\pi\iota$.

§ 9. Suppose in the first place that $\mathfrak{R}(x) > 0$. Then we have the following lemma* :—

If $|\arg x| < \pi/2$, the integral $\frac{1}{2\pi\iota}\int \frac{x^s\Gamma(-s)}{(s+\theta)^{\beta}}ds$ vanishes when taken along any part of the great circle at infinity for which $\mathfrak{R}(s) > -l$, where l is any finite positive quantity, provided the circle pass between the points $s = n$, n being a positive integer.

The same integral is finite when taken along any parallel to the imaginary axis in the finite part of the plane, which does not pass through finite singularities of the subject of integration.

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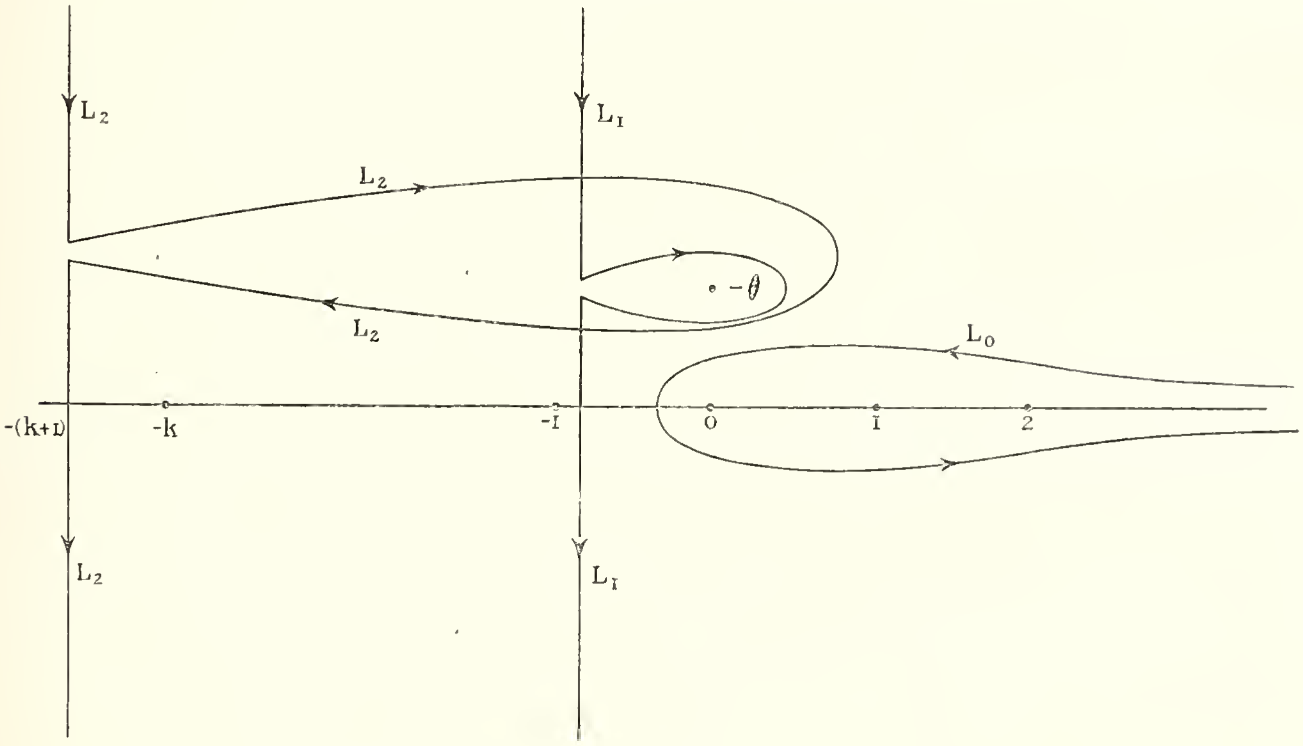
* With this theorem the reader may compare the method used by the author to obtain the asymptotic expansion of the multiple gamma function. 'Cambridge Philosophical Transactions,' vol. 19, §§ 55–57.

The second part of the theorem is true, since when $s = u + \iota v$ and $|v|$ is very large, $|\Gamma(-s)|$ behaves like $\exp\left\{-\frac{\pi}{2}|v|\right\}$.

The first part follows from this fact in combination with the asymptotic expansion of $\Gamma(-s)$ for complex values of s.

§ 10. If L_1 be a contour parallel to the imaginary axis and cutting the real axis between $s = 0$ and $s = -1$, the contour, if necessary, having a loop to ensure that $-\theta$ is to its left as in the figure, then

$$G_\beta(-x;\theta) = -\frac{1}{2\pi\iota}\int_{L_1}\frac{x^s\Gamma(-s)}{(s+\theta)^\beta}\,ds.$$



For by the lemma we may bend the contour round until it becomes the contour L_0 of the figure.

The residue of the subject of integration at $s = n$ is

$$\underset{\epsilon=0}{Lt} - \frac{x^n}{(n+\theta)^\beta}\,\epsilon\Gamma(-n-\epsilon) = \frac{(-x)^n}{(n+\theta)^\beta\,\Gamma(n+1)}.$$

Hence by CAUCHY'S theorem we have the proposition stated.

§ 11. Let L_2 be a contour parallel to the imaginary axis (except for a loop round $-\theta$) which cuts the real axis in $s = -\lambda$ between $s = -k$ and $s = -(k+1)$, then

$$G_\beta(-x;\theta) = -\frac{1}{2\pi\iota}\int_{L_2}\frac{x^s\Gamma(-s)}{(s+\theta)^\beta}\,ds.$$

This follows from CAUCHY'S theorem combined with the second part of the lemma.

§ 12. The integral along the straight parts of the contour may be denoted by I_k.

It is evident that $|x^k \mathrm{I}_k|$ tends to zero as $|x|$ tends to infinity for any finite value of k.

In the remaining part of the integral put $s+\theta = -y$ and we find

$$\mathrm{G}_\beta(-x\,;\theta) = -\frac{x^{-\theta}}{2\pi\iota}\int_{\mathrm{C}_\lambda}(-y)^{-\beta}x^{-y}\Gamma(y+\theta)\,dy+\mathrm{I}_k,$$

the integral being taken round a contour C_λ, which encloses the origin and embraces the positive half of the real axis up to the point $\lambda-\mathfrak{R}(\theta)$.

The poles of $\Gamma(y+\theta)$ are at the points $-\theta-r$, $r = 0, 1, 2, \ldots \infty$.

Hence, within a circle of radius equal to the minimum value of $|\theta+r|$, it admits the convergent expansion

$$\sum_{r=0}^{\infty}\frac{\Gamma^{(r)}(\theta)\,y^r}{r\,!}.$$

I will show that $\mathrm{G}_\beta(-x\,;\theta)$ admits the asymptotic expansion

$$\sum_{r=0}^{\infty}\frac{\iota}{2\pi}x^{-\theta}\int\frac{(-)^r\,\Gamma^{(r)}(\theta)}{r\,!}(-y)^{r-\beta}e^{-y\log x}\,dy,$$

the integrals being taken round a gamma-function contour which encloses the origin, embraces the real axis, and passes from positive infinity to positive infinity again.

This expansion may evidently be written

$$x^{-\theta}\sum_{r=0}^{\infty}\frac{(-)^r\,\Gamma^{(r)}(\theta)}{r\,!\,\Gamma(\beta-r)(\log x)^{r-\beta+1}}.$$

We have, if m be a finite positive integer,

$$\mathrm{G}_\beta(-x\,;\theta)-\mathrm{I}_k-x^{-\theta}\sum_{r=0}^{m}\frac{(-)^r\,\Gamma^{(r)}(\theta)}{r\,!\,\Gamma(\beta-r)(\log x)^{r-\beta+1}}$$

$$=\frac{\iota}{2\pi}x^{-\theta}\int_{\mathrm{C}_\lambda}(-y)^{-\beta}x^{-y}\left[\Gamma(y+\theta)-\sum_{r=0}^{m}\frac{\Gamma^{(r)}(\theta)}{r\,!}y^r\right]dy-\sum_{r=0}^{m}\frac{\sin\pi\beta}{\pi}\int_{\lambda-\mathfrak{R}(\theta)}^{\infty}y^{-\beta+r}x^{\theta-y}\frac{\Gamma^{(r)}(\theta)}{r\,!}dy\,.\ (1),$$

the latter integrals being taken along the positive half of the real axis.

If we denote the sum of these integrals by J, we readily see that, for any finite value of m, we can by taking $|x|$ sufficiently large make $|\mathrm{J}x^k|$ as small as we please.

§ 13. We have now to consider the first integral in (1).

Let η be a point on the positive half of the real axis just within the circle of convergence of $\Gamma(y+\theta)$, so that $|\eta| <$ the minimum value of $|\theta+n|$, $n = 0, 1, 2, \ldots \infty$.

Then the first integral in question can be split up into two others, I_1 and I_2 (say). We denote by I_1 the integral round a contour M (say), enclosing the origin and passing from the point η to this point again, η being on the cross-cut which renders the subject of integration uniform. The remaining integral I_2 will be equal to

$$\frac{\sin\pi\beta}{\pi}x^{-\theta}\int_{\eta}^{\lambda-\mathfrak{R}(\theta)}y^{-\beta}x^{-y}\left\{\Gamma(y+\theta)-\sum_{r=0}^{m}\frac{\Gamma^{(r)}(\theta)\,y^r}{r\,!}\right\}dy.$$

If ${}_mG_k$ be the maximum value of

$$\left|\frac{\sin \pi\beta}{\pi} y^{-\beta}\left\{\Gamma(y+\theta) - \sum_{r=0}^{m} \frac{\Gamma^{(r)}(\theta)\, y^r}{r!}\right\}\right|$$

on this line, we shall have

$$|I_2| < {}_mG_k\, |x^{-\theta-\eta}| \quad |\lambda - \mathfrak{R}(\theta) - \eta|.$$

Thus for all finite values of k and m, however large, we can take $|x|$ so large that $|x^{\theta+\eta-\epsilon} I_2|$, where $\epsilon > 0$ and as small as we please, tends to zero as nearly as we please.

Finally the integral I_1

$$= \frac{\iota}{2\pi} x^{-\theta} \int_{M} (-y)^{-\beta} x^{-y} \left\{\sum_{r=m+1}^{\infty} \frac{\Gamma^{(r)}(\theta)}{r!} y^r\right\} dy.$$

By the substitution $\eta = y \log x$, we see exactly as in § 5 that $|I_1 x^{\theta} (\log x)^{-\beta+1+m}|$ can be made as small as we please by taking $|x|$ sufficiently large.

Hence

$$|x^{\theta} (\log x)^{-\beta+1+m}| \quad \left| G_\beta(-x\,;\theta) - x^{-\theta} \sum_{r=0}^{m} \frac{(-)^r\, \Gamma^{(r)}(\theta)}{r!\, \Gamma(\beta-r)\, (\log x)^{r-\beta+1}}\right|$$

can for any finite value of m be made as small as we please by taking $|x|$ sufficiently large.

Therefore, provided $\mathfrak{R}(x) < 0$ and θ is not real and negative, we have the asymptotic expansion

$$G_\beta(x\,;\theta) = (-x)^{-\theta} [\log(-x)]^{\beta-1} \sum_{r=0}^{\infty} \frac{(-)^r\, \Gamma^{(r)}(\theta)}{\Gamma(r+1)\, \Gamma(\beta-r)\, \{\log(-x)\}^r},$$

the principal value of $\log(-x)$, which is real when x is real and negative, being taken.

§ 14. We proceed now to obtain the asymptotic expansion of

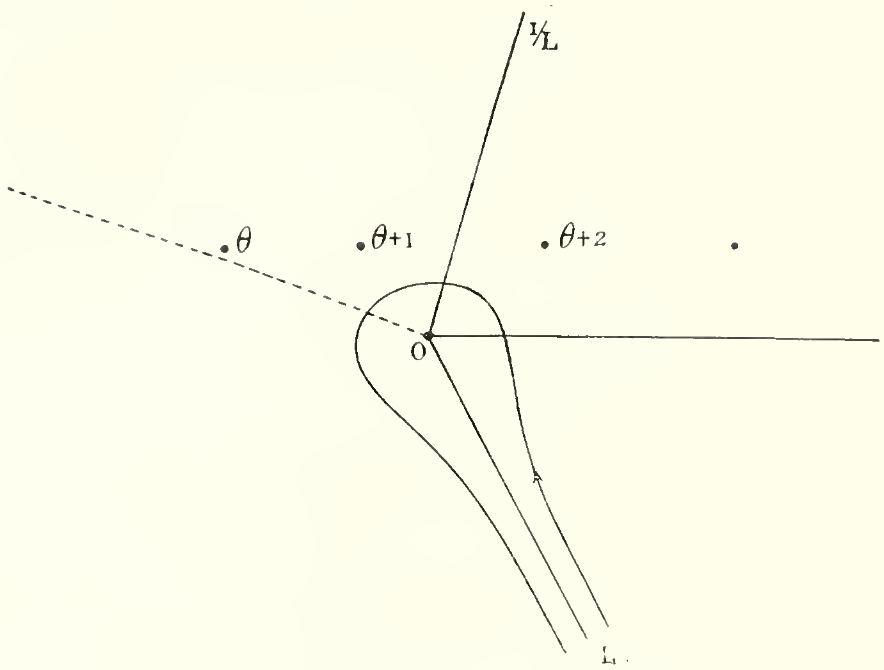
$$G_\beta(x\,;\theta) = \sum_{n=0}^{\infty} x^n / n!\, (n+\theta)^{\beta}$$

in the case in which $\mathfrak{R}(x) > 0$.

We will assume that θ is not real and negative. In this case the points θ, $\theta+1$, $\theta+2$, ... all lie within an angle, vertex the origin, which is less than π.

Let the bisector of this angle be the line $1/L$, and let L be the image of this line in the real axis. The figure is drawn for the case in which the imaginary part of θ is positive.

Suppose now that $(-z)^{\beta-1} = \exp\{(\beta-1)\log(-z)\}$ when the logarithm is rendered one-valued by a cross-cut along the axis L, and $\log(-z)$ is such that it is real when z is real and negative.



Then*

$$\frac{\iota\Gamma(1-\beta)}{2\pi}\int_{L}(-z)^{\beta-1}e^{-(\theta+n)z}\,dz=(\theta+n)^{-\beta}$$

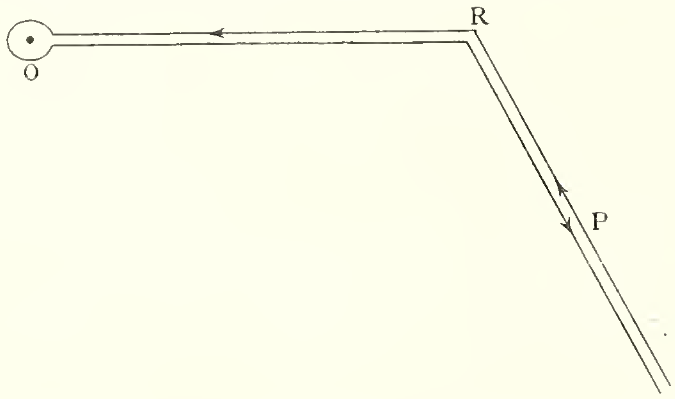
when the integral is taken along a contour, as in the figure, embracing the axis L, and $(\theta+n)^{-\beta}=\exp[-\beta\log(\theta+n)]$, the logarithm being rendered one-valued by a cross-cut along the negative direction of the axis of 1/L, and $\log(\theta+n)$ being real when $\theta+n$ is real and positive. It is a value of $(\theta+n)^{-\beta}$ so defined which we suppose to intervene in the fundamental series by which $G_{\beta}(x;\theta)$ is defined. [*Vide* § 8.]

We now have

$$G_{\beta}(x;\theta)=\frac{\iota\Gamma(1-\beta)}{2\pi}\int_{L}(-z)^{\beta-1}\sum_{n=0}^{\infty}\frac{x^{n}}{n!}e^{-(\theta+n)z}\,dz$$

$$=\frac{\iota\Gamma(1-\beta)}{2\pi}\int_{L}(-z)^{\beta-1}\exp\{-z\theta+e^{-z}x\}\,dz.$$

§ 15. We may deform the original contour L till it has the position of the figure.



It thus consists of a small curcuit round the origin, the real axis from 0+ to R described both ways and a line P from R to ∞ parallel to the original direction of the axis of the contour which is also described both ways. We suppose that the cross-cut which renders $(-z)^{\beta-1}$ uniform has been deformed with the contour.

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* 'M. G. F.,' p. 388. [In this manner reference will be made to the paper cited in § 9.]

The value of the integral in the two directions along the final line P is, putting $z = \mathrm{R}+\zeta$,

$$\mathrm{I}_2 = \frac{1}{\Gamma(\beta)}\int_0^{\infty}(\mathrm{P})\,(\mathrm{R}+\zeta)^{\beta-1}\exp\{-\mathrm{R}\theta-\zeta\theta+e^{-\mathrm{R}-\zeta}x\}\,d\zeta,$$

the principal value of $(\mathrm{R}+\zeta)^{\beta-1}$, which has a cross-cut along the negative half of the real axis, being taken. The integral is a line integral along P.

On this line $\mathfrak{R}(\zeta) > 0$. Hence the maximum value of the real part of $e^{-\mathrm{R}-\zeta}x$ is $e^{-\mathrm{R}}|x|\mathrm{K}$, where K is a finite quantity independent of R and $|x|$.

Hence

$$|\mathrm{I}_2| < \frac{1}{\Gamma(\beta)}\exp\{e^{-\mathrm{R}}|x|\mathrm{K}-\mathrm{R}\mathfrak{R}(\theta)\}\,|\mathrm{R}^{\beta-1}|$$
$$\times\int_0^{\infty}(\mathrm{P})\left|\left(1+\frac{\zeta}{\mathrm{R}}\right)^{\beta-1}\right|\,|\exp(-\theta\zeta)|\,|d\zeta|.$$

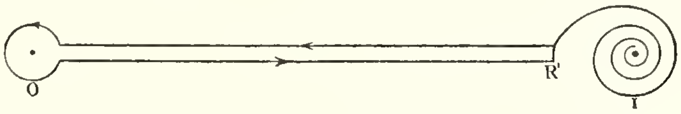
The last integral is convergent and tends to a definite finite value Q as R increases.

When $|x|$ is large let us take $|x| = e^{\mathrm{R}}$. Then

$$|\mathrm{I}_2| < \frac{1}{\Gamma(\beta)}\exp\mathrm{K}\,\{\log|x|\}^{\mathfrak{R}(\beta)-1}\,\frac{\mathrm{Q}}{|x|^{\mathfrak{R}(\theta)}}.$$

When $\mathfrak{R}(\theta) > 0$, $|\mathrm{I}_2|$ will obviously tend to zero as R tends to infinity, and this is true of $|e^{-x}\mathrm{I}_2|$ for all values of θ which are not real and negative, if $\mathfrak{R}(x) > 0$.

§ 16. We have now to consider the value of the original integral along the contour which consists of the small circuit round the origin and the real axis described both ways from $0+$ to R. We denote this integral by I_1. Make the transformation $1-y = e^{-z}$. Then corresponding to the original modified contour we have a new contour Q as in the figure. This consists of a small circuit round the origin and the



real axis described both ways from $0+$ to R′, where $\mathrm{R}' = 1-e^{-\mathrm{R}}$. The former line P from R to ∞ becomes an infinite spiral from R′ round the point 1 up to this point, the whole spiral being contained within a circle of radius $e^{-\mathrm{R}}$.

We now have

$$\mathrm{I}_1 = e^{x}\frac{\iota\Gamma(1-\beta)}{2\pi}\int_{\mathrm{Q}}[\log(1-y)]^{\beta-1}(1-y)^{\theta-1}e^{-xy}\,dy,$$

the integral being taken round the origin from R′ back to R′. The many-valued functions which intervene in the subject of integration are such that, when $|y| < 1$,

$$[\log(1-y)]^{\beta-1}(1-y)^{\theta-1} = (-y)^{\beta-1}\sum_{n=0}^{\infty}c_n(-y)^n \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

the principal value of $(-y)^{\beta-1}$, which is real when y is real and negative and has a cross-cut along the line joining 0 and 1, being taken.

Evidently $c_0 = 1$. For the evaluation of the other coefficients of the expansion the reader may refer to a paper by FÉRAND.*

Now

$$e^x \frac{\iota\Gamma(1-\beta)}{2\pi}\int_Q c_n(-y)^{n+\beta-1}e^{-xy}\,dy$$

$$= e^x \frac{\iota\Gamma(1-\beta)}{2\pi}\int_G c_n(-y)^{n+\beta-1}e^{-xy}\,dy - \frac{(-)^n}{\Gamma(\beta)}\int_{1-e^{-R}}^{\infty} c_n y^{\beta+n-1}e^{x(1-y)}\,dy,$$

where G is a gamma-function contour enclosing the origin and embracing the positive half of the real axis and the second line integral is taken along the real axis.

Therefore

$$e^x \frac{\iota\Gamma(1-\beta)}{2\pi}\int_Q c_n(-y)^{n+\beta-1}e^{-xy}\,dy = e^x \frac{c_n\Gamma(1-\beta)}{\Gamma(1-\beta-n)\,x^{\beta+n}} - J_n,$$

where $|J_n| < K'_n|\exp\{e^{-R}x\}| < K'_n|\exp\cos(\arg x)|$, and K'_n is a finite positive quantity for all finite values of n.

Hence

$$I_1 - e^x \sum_{n=0}^{k-1} \frac{c_n\Gamma(1-\beta)}{\Gamma(1-\beta-n)\,x^{n+\beta}} = e^x \frac{\iota\Gamma(1-\beta)}{2\pi}\int_Q \left[\sum_{n=k}^{\infty} c_n(-y)^{\beta+n-1}\right] e^{-xy}\,dy - \sum_{n=0}^{k-1} J_n.$$

But as in § 5 we see that

$$\left| x^{\beta+k-1}\int_Q \left[\sum_{n=k}^{\infty} c_n(-y)^{\beta+n-1}\right] e^{-xy}\,dy \right|$$

can be made as small as we please for any assigned value of k by taking $|x|$ sufficiently large.

Hence, when $\mathfrak{R}(x) > 0$, $e^{-x}I_1$ admits the asymptotic expansion

$$\sum_{n=0}^{\infty} \frac{c_n\Gamma(1-\beta)}{\Gamma(1-\beta-n)\,x^{\beta+n}}.$$

Reverting to the value which we obtained as the quantity greater than $|I_2|$, we see that $e^{-x}G_\beta(x;\theta)$ admits, when $\mathfrak{R}(x) > 0$, the same asymptotic expansion.

§ 17. In the foregoing investigation θ may have any finite value while not real and negative (zero included).

But the expansion is valid even if θ be real and negative, provided it be not a negative integer.

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* FÉRAND, "Bordeaux Procès Verbaux," 1896–97, pp. 93–97; quoted in the 'Fortschritte der Mathematik,' vol. 29, p. 375.

For if θ lie between $-k$ and $-(k+1)$, k being a positive integer, we consider $G_\beta(x;\theta+k)$.

By the theorem just proved, $G_\beta(x;\theta+k)$ admits an asymptotic expansion.

Also $G_\beta(x;\theta+k) = \dfrac{d^k}{dx^k}\left[G_\beta(x;\theta) - \sum\limits_{n=0}^{k-1}\dfrac{x^n}{\Gamma(n+1)(n+\theta)^\beta}\right]$.

Hence, since by a theorem due to POINCARÉ, we may integrate an asymptotic series, the general result follows.*

Finally we see that, if $\mathfrak{R}(x) > 0$, and θ be not zero or a negative integer, the function $G_\beta(x;\theta)$ admits the asymptotic expansion

$$\frac{e^x}{x^\beta}\sum_{n=0}^{\infty}\frac{c_n\Gamma(1-\beta)}{\Gamma(1-\beta-n)\,x^n}.$$

The coefficients c_n are determined by the expansion

$$\left[\frac{\log(1-y)}{-y}\right]^{\beta-1}(1-y)^{\theta-1} = \sum_{n=0}^{\infty}c_n(-y)^n, \quad \text{valid where } |y| < 1.$$

§ 18. But when $\mathfrak{R}(x) < 0$, we have also obtained an asymptotic expansion, and the restriction that θ shall not be real and negative can be replaced by the restriction that θ shall not be zero or a negative integer.

Combining the two results we see that, when $|x|$ is large and θ not zero or a negative integer, the behaviour of $G_\beta(x;\theta)$ is given by the sum of the two asymptotic expansions

$$\frac{e^x}{x^\beta}\sum_{n=0}^{\infty}\frac{c_n\Gamma(1-\beta)}{\Gamma(1-\beta-n)\,x^n} + (-x)^{-\theta}[\log(-x)]^{\beta-1}\sum_{n=0}^{\infty}\frac{(-)^n\Gamma^{(n)}(\theta)}{\Gamma(n+1)\,\Gamma(\beta-n)\{\log(-x)\}^n} \quad \text{(A)}.$$

This double expansion is valid for all values of arg x between $-\pi$ and π, except possibly those for which $|\arg x| = \dfrac{\pi}{2}$. It is, as we shall see later, true even in these cases.

§ 19. When $\beta=1$, the function reduces to $G(x;\theta) = \sum\limits_{n=0}^{\infty}\dfrac{x^n}{\Gamma(n+1)(n+\theta)}$, which was previously considered.

The c's are now determined by the expansion $(1-y)^{\theta-1} = \sum\limits_{n=0}^{\infty}c_n(-y)^n$.

Therefore $c_n = (\theta-1)(\theta-2)\ldots(\theta-n)/n\,!$

The asymptotic formula (A) therefore reduces to

$$\frac{e^x}{x}\sum_{n=0}^{\infty}\frac{(-)^n(\theta-1)\ldots(\theta-n)}{x^n} + (-x)^{-\theta}\Gamma(\theta),$$

which was the result previously obtained (§ 6, III.).

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* The matter does not seem of sufficient importance for an elaborate proof. I may, however, refer the reader to Mr. HARDY'S paper, p. 419 (*loc. cit.*, § 2).

§ 20. We have obtained the asymptotic expansion of $G_\beta(x;\theta)$ in the two cases when $\mathfrak{R}(x) > 0$ and when $\mathfrak{R}(x) < 0$ by separate methods. By this, however, we are left in doubt as to the behaviour of the function on the imaginary axis. We proceed now to obtain the two expansions simultaneously.

We shall limit ourselves to the case $\mathfrak{R}(\theta) > 0$, as the result can then be extended to all values of θ, except those which are zero or a negative integer.

As previously, we have

$$G_\beta(x;\theta) = \frac{\iota\Gamma(1-\beta)}{2\pi}\int_L (-z)^{\beta-1}\exp\{-z\theta+e^{-z}x\}\,dz,$$

where now, since $\mathfrak{R}(\theta) > 0$, the contour L can be taken to embrace the positive half of the real axis.

Hence

$$G_\beta(x;\theta) = \frac{\iota\Gamma(1-\beta)}{2\pi}\int (-z)^{\beta-1}\exp\{-z\theta+e^{-z}x\}\,dz + \frac{1}{\Gamma(\beta)}\int_\eta^\infty z^{\beta-1}\exp\{-z\theta+e^{-z}x\}\,dz.$$

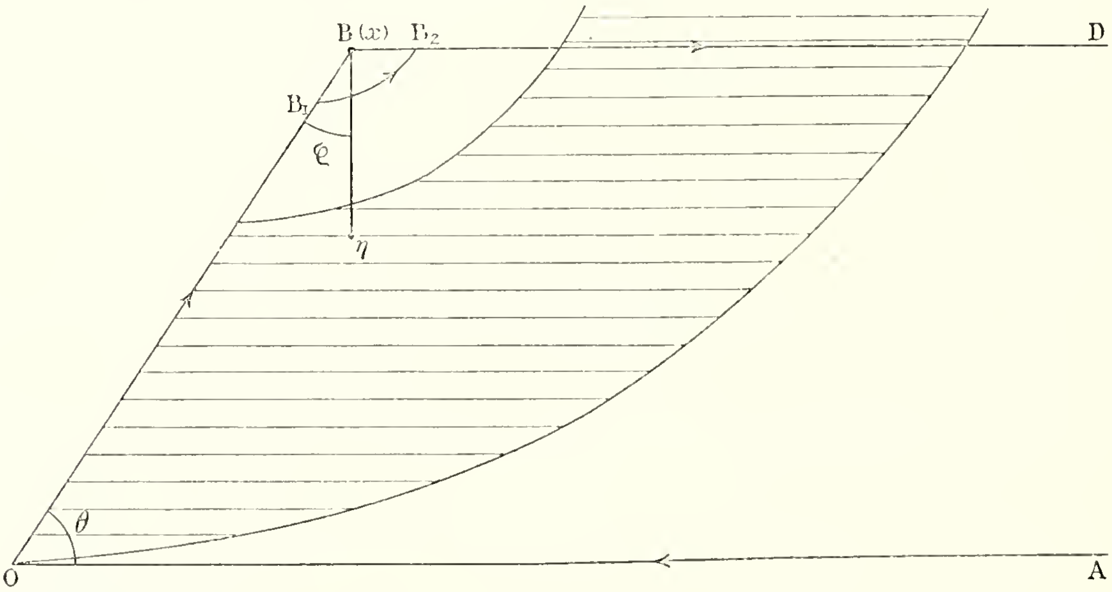
The first integral is taken round a circle of radius η surrounding the origin, beginning and ending on the positive half of the real axis, which is a cross-cut to render $(-z)^{\beta-1}$ uniform. The second integral is taken along the real axis.

If $\mathfrak{R}(\beta) > 0$, the first integral vanishes as η approaches zero. For simplicity we consider only this case. The limitation simplifies the statement of the proof: its absence does not affect the argument.

By the substitution $1-y/x = e^{-z}$, we now obtain

$$\Gamma(\beta)\,G_\beta(x;\theta) = \frac{1}{x}\int_0^x \left[-\log\left(1-\frac{y}{x}\right)\right]^{\beta-1}\left(1-\frac{y}{x}\right)^{\theta-1} e^{x-y}\,dy,$$

the integral being taken along the straight line from O, the origin, to B, the point x.



Take now the integral

$$\int\left[-\log\left(1-\frac{y}{x}\right)\right]^{\beta-1}\left(1-\frac{y}{x}\right)^{\theta-1} e^{x-y}\,dy$$

round the contour AOB_1B_2D of the figure. This contour consists of the real axis from A $(+\infty)$ to O, the origin, the line OB_1, a circular arc B_1B_2 of radius ϵ round B as centre, and the line B_2D, which passes to infinity parallel to OA.

If we take throughout that value of $\left[-\log\left(1-\frac{y}{x}\right)\right]^{\beta-1}\left(1-\frac{y}{x}\right)^{\theta-1}$ which is one-valued on the plane dissected by a cross-cut drawn away from the origin from B to infinity, and which is therefore represented in this region by the series (summable and divergent when $|y|>|x|$) $\left(\frac{y}{x}\right)^{\beta-1}\sum_{n=0}^{\infty} c_n\left(-\frac{y}{x}\right)^n$, we may use CAUCHY'S theorem.

We thus see that

$$G_\beta(x;\theta) = \frac{1}{x\Gamma(\beta)}\int_0^\infty \left[-\log\left(1-\frac{y}{x}\right)\right]^{\beta-1}\left(1-\frac{y}{x}\right)^{\theta-1} e^{x-y}\,dy$$

$$-\frac{1}{x\Gamma(\beta)}\int_\epsilon^\infty \left[-\log\left(-\frac{\eta}{x}\right)\right]^{\beta-1}\left(-\frac{\eta}{x}\right)^{\theta-1} e^{-\eta}\,d\eta+I_3.$$

The integral I_3 is the integral round the arc B_1B_2. It vanishes in the limit when $\epsilon=0$, since $\mathfrak{R}(\theta)>0$. The two line integrals are taken along OA and B_2D respectively parallel to the positive half of the real axis. In the second integral we have made the substitution $\eta=y-x$.

The first integral by the general theorem of § 5 admits the asymptotic expansion

$$\frac{e^x}{x^\beta}\sum_{n=0}^{\infty}\frac{(-)^n c_n\Gamma(\beta+n)}{\Gamma(\beta)\,x^n}.$$

§ 21. We proceed to consider the second integral.

We have to seek to find on BD the value of $\log[-\log(-\eta/x)]$ which on OB admitted the expansion

$$\log\left[-\log\left(1-\frac{y}{x}\right)\right] = \log\frac{y}{x}+(\ldots)\frac{y}{x}+\ldots,$$

and which is represented by the continuation of this summable divergent series.

Let $x=re^{\iota\theta}$, so that, its principal value being taken, $\log(-x)=\log r+\iota(\theta-\pi)$ θ being the angle of the figure. Let $\eta=\rho e^{\iota(\phi+\theta-\pi)}$, so that ϕ is the angle given in the figure. We assume that r is large, and consider the shaded area bounded by $\rho=1$ and $\rho=r$.

When $-\eta/x$ is real and positive, $|\eta|$ being less than $|x|$, $\log[-\log(-\eta/x)]$ is real. We will show that, for values of η on B_2D within the shaded area, we must take

$$\log\left[-\log\left(-\frac{\eta}{x}\right)\right] = \log\{\log r+\iota(\theta-\pi)\}+\log\left[1-\frac{\log\rho+\iota(\theta+\phi-\pi)}{\log r+\iota(\theta-\pi)}\right] \quad . \quad (2),$$

where, within the shaded area, the final logarithm is such that

$$\exp\left[(\beta-1)\log\left\{1-\frac{\log\rho+\iota(\theta+\phi-\pi)}{\log r+\iota(\theta-\pi)}\right\}\right]$$

admits the expansion

$$\sum_{n=0}^{\infty} \frac{(-)^n \Gamma(\beta)}{\Gamma(\beta-n)\, n\,!} \left[\frac{\log \rho + \iota(\theta+\phi-\pi)}{\log r + \iota(\theta-\pi)}\right]^n .$$

Evidently the only trouble which arises is with the specification of the imaginary parts of the logarithms. Now when r is large and $r > \rho > 1$, the imaginary part of $\log[-\log(-\eta/x)] = \log[\log r/\rho - \iota\phi]$ is $-\tan^{-1}\{\phi/(\log r/\rho)\}$, the principal value of the inverse tangent which lies between 0 and $\pi/2$ being taken.

The imaginary part of $\log(\log r + \iota\overline{\theta-\pi})$ is similarly $-\tan^{-1}\{(\pi-\theta)/\log r\}$, the inverse tangent again lying between 0 and $\pi/2$.

Also the imaginary part of $\log\left[1 - \dfrac{\log \rho + \iota(\theta+\phi-\pi)}{\log r + \iota(\theta-\pi)}\right]$ when the value is taken which is represented within the shaded area by the series

$$-\sum_{n=0}^{\infty} \frac{1}{n} \left[\frac{\log \rho + \iota(\theta+\phi-\pi)}{\log r + \iota(\theta-\pi)}\right]^n$$

is also negative and lies between 0 and $\pi/2$.

When r is large and ρ is just greater than unity, all three imaginary parts are very small. The equality (2) is therefore established.

§ 22. We see then that within that part of BD which is within the shaded area

$$\left[-\log\left(-\frac{\eta}{x}\right)\right]^{\beta-1} = [\log(-x)]^{\beta-1} \left\{\sum_{n=0}^{\infty} \frac{(-)^n \Gamma(\beta)}{\Gamma(\beta-n)\, n!} \left[\frac{\log \eta}{\log(-x)}\right]^n\right\}$$

the principal values of $\log \eta$ and $\log(-x)$ being taken. And on the remainder of BD between ϵ and ∞ the expansion continues to hold as one which is divergent but summable. [An exceptional case occurs when x is real and negative, when a slight modification of the contour must be taken to avoid the point O.]

Therefore, by the fundamental theorem of § 5, we have, when $\mathfrak{R}(\theta) > 0$, for the asymptotic expansion of the second integral,

$$\sum_{n=0}^{\infty} (-x)^{-\theta} \int_{\epsilon}^{\infty} e^{-y} y^{\theta-1} \sum_{n=0}^{\infty} \frac{(-)^n [\log y]^n}{\Gamma(\beta-n)\,\Gamma(n+1)\,[\log(-x)]^{n+1-\beta}}\, dy$$

$$= (-x)^{-\theta} [\log(-x)]^{\beta-1} \sum_{n=0}^{\infty} \frac{(-)^n \Gamma^{(n)}(\theta)}{\Gamma(n+1)\,\Gamma(\beta-n)\,[\log(-x)]^n} .$$

Finally, therefore, if $\mathfrak{R}(\theta) > 0$, we have $G_\beta(x;\theta)$ represented by the sum of the two asymptotic expansions

$$\frac{e^x}{x^\beta} \sum_{n=0}^{\infty} \frac{(-)^n c_n \Gamma(\beta+n)}{\Gamma(\beta)\, x^n} + (-x)^{-\theta} [\log(-x)]^{\beta-1} \sum_{n=0}^{\infty} \frac{(-)^n \Gamma^{(n)}(\theta)}{n!\,\Gamma(\beta-n)\,[\log(-x)]^n} .$$

This result is valid for all values of arg x, with the assigned prescription for $\log(-x)$.

The Asymptotic Behaviour of $G_\beta(x;\theta)$, *when* $\mathfrak{R}(x) > 0$, *and* β *tends to Infinity.*

§ 23. The previous asymptotic expansions give us no indication of the behaviour of $G_\beta(x;\theta)$ when β grows indefinitely, and $\mathfrak{R}(x) > 0$. For although we have seen that, so long as β is finite,

$$G_\beta(x;\theta) = e^x \frac{J(x)}{x^\beta},$$

where $|J(x)|$ tends to a definite finite limit when $|x|$ grows indefinitely, yet as β tends to infinity it is possible that $|J(x)|$ will also grow indefinitely. This possibility must now be examined.

§ 24. We base our investigation on the properties of the function

$$S(s) = \sum_{n=0}^{\infty} \frac{\Gamma(n-s)}{\Gamma(n+1)(n+\theta)^\beta}.$$

The series is convergent if $\mathfrak{R}(\beta+s) > 0$. For, if $\sigma = -s-1$, the general term is equal to

$$\frac{\Gamma(n+\sigma+1)}{\Gamma(n+1)(n+\theta)^\beta} = \frac{\Gamma(\sigma+1)\left\{\left(1+\frac{\sigma}{1}\right)e^{-\frac{\sigma}{1}}\right\}\ldots\left\{\left(1+\frac{\sigma}{n}\right)e^{-\frac{\sigma}{n}}\right\}}{\exp\left\{-\sigma\left(\frac{1}{1}+\ldots+\frac{1}{n}\right)\right\}(n+\theta)^\beta}$$

$$= \frac{\exp\left[\sigma\left\{\frac{1}{1}+\ldots+\frac{1}{n}\right\}\right]e^{-\gamma\sigma}}{\prod_{r=n+1}^{\infty}\left[\left(1+\frac{\sigma}{r}\right)e^{-\frac{\sigma}{r}}\right](n+\theta)^\beta}$$

$$= \frac{\exp\theta_n}{\prod_{r=n+1}^{\infty}\left[\left(1+\frac{\sigma}{r}\right)e^{-\frac{\sigma}{r}}\right]n^{\beta-\sigma}\left(1+\frac{\theta}{n}\right)^\beta},$$

where θ_n tends to zero and n tends to infinity.

Thus, however large the imaginary part of σ may be (even if it is infinite), the series will be absolutely convergent provided $\mathfrak{R}(\beta-\sigma-1) > 0$, that is to say, provided $\mathfrak{R}(\beta+s) > 0$.

The following argument would have been more simple; it would not however have brought out so clearly that the imaginary part of σ may be infinite.

If u_n denote the nth term of the series,

$$\frac{u_{n+1}}{u_n} = \frac{n-s}{n+1}\left(\frac{n+\theta}{n+\theta+1}\right)^\beta = 1-(\beta+s+1)/n+(\ldots)/n^2+\ldots$$

Hence, by a known theorem, the series is convergent if $\mathfrak{R}(\beta+s+1) > 1$.

§ 25. *We will now show that, if* $\mathfrak{R}(\beta+s) > 0$, *and* $\mathfrak{R}(\theta) > 0$,

$$\frac{S(s)}{\Gamma(-s)} = \frac{1}{\Gamma(\beta)}\int_0^\infty y^{\beta-1}e^{-\theta y}(1-e^{-y})^s\,dy,$$

the integration being taken along the positive half of the real axis.

Let $(1-e^{-y})^s = \sum\limits_{n=0}^{N-1}\frac{(-s)\dots(-s+n-1)}{1\,.\,2\dots n}\,e^{-ny}+\mathfrak{R}_N$.

Then, if $y \geqq 0$, and $\mathfrak{R}(s) > 0$, and, as before, $\sigma = -s-1$,

$$|\mathfrak{R}_N| = \left|\sum_{n=N}^{\infty}\frac{(-s)\dots(-s+n-1)}{n\,!}\,e^{-ny}\right| \leqq \sum_{n=N}^{\infty}\left|\frac{\prod\limits_{r=1}^{n}\left[\left(1+\frac{\sigma}{r}\right)e^{-\frac{\sigma}{r}}\right]e^{-ny}}{\exp\left\{-\sigma\left(\frac{1}{1}+\dots+\frac{1}{n}\right)\right\}}\right|.$$

Now $\left|e^{\gamma\sigma}\prod\limits_{r=1}^{n}\left[\left(1+\frac{\sigma}{r}\right)e^{-\frac{\sigma}{r}}\right]\right|$ tends to a definite finite limit as n tends to infinity. Let μ be its maximum value when $n \geqq N$.

Then $|\mathfrak{R}_N| \leqq \mu\sum\limits_{n=N}^{\infty}e^{-ny}\left|n^{\sigma(1+\epsilon_n)}\right|$, where ϵ_n tends to zero as n tends to infinity.

Hence, if $y \geqq 0$, $|\mathfrak{R}_N| \leqq Ke^{-Ny}$, if $\mathfrak{R}(s) > 0$, where K is a definite finite quantity independent of N and y.

Hence, if $I_N = \int_0^\infty y^{\beta-1}e^{-\theta y}\,\mathfrak{R}_N(y)\,dy$,

$$|I_N| \leqq K\int_0^\infty y^{\mathfrak{R}(\beta-1)}e^{-y\{N+\mathfrak{R}(\theta)\}}\,dy.$$

Thus I_N tends to zero as N tends to infinity if $\mathfrak{R}(\beta) > 0$ and $\mathfrak{R}(s) > 0$.

Now

$$\begin{aligned}\frac{1}{\Gamma(\beta)}\int_0^\infty y^{\beta-1}e^{-\theta y}(1-e^{-y})^s\,dy &= \frac{1}{\Gamma(\beta)}\int_0^\infty y^{\beta-1}e^{-\theta y}\sum_{n=0}^{N-1}\frac{(-s)\dots(-s+n-1)}{n\,!}\,e^{-ny}+I_N\\ &= \frac{1}{\Gamma(-s)\,\Gamma(\beta)}\sum_{n=0}^{N-1}\int y^{\beta-1}\,\frac{\Gamma(n-s)}{n\,!}\,e^{-(n+\theta)y}\,dy+I_N\\ &= \frac{1}{\Gamma(-s)}\sum_{n=0}^{N-1}\frac{\Gamma(n-s)}{n\,!\,(n+\theta)^\beta}+I_N \text{ if } \mathfrak{R}(\beta) > 0.\end{aligned}$$

Make now N tend to infinity, and we see that, if $\mathfrak{R}(\beta) > 0$ and $\mathfrak{R}(s) > 0$,

$$S(s) = \frac{\Gamma(-s)}{\Gamma(\beta)}\int_0^\infty y^{\beta-1}e^{-\theta y}(1-e^{-y})^s\,dy.$$

But both sides of this equality are continuous and finite except for the poles of $\Gamma(-s)$, if $\mathfrak{R}(\theta) > 0$ and $\mathfrak{R}(\beta+s) > 0$. Therefore the equality holds under this limitation.

§ 26. *We will next show that, if* $s = u+\iota v$ *and* $\mathfrak{R}(\beta+s)>0$, *when* $|v|$ *is very large,* $|S(s)| < Ke^{-\frac{1}{2}\pi|v|}$, *where* K *is a finite quantity independent of* v.

For, if $\mathfrak{R}(\theta)>0$,

$$\left|\frac{S(s)}{\Gamma(-s)}\right| = \left|\frac{1}{\Gamma(\beta)}\int_0^\infty y^{\beta-1}e^{-\theta y}(1-e^{-y})^{u+\iota v}\,dy\right| < \left|\frac{1}{\Gamma(\beta)}\right|\int_0^\infty |y^{\beta-1}e^{-\theta y}|(1-e^{-y})^{u}\,dy < K,$$

where K is a definite finite quantity independent of v.

But, when $|v|$ tends to infinity, $|\Gamma(-s)|/e^{-\frac{1}{2}\pi|v|}$ tends to a definite finite limit. We therefore have the given theorem if $\mathfrak{R}(\theta)>0$.

When $\mathfrak{R}(\theta) \not> 0$, we can, if $|\theta|$ be finite, find a finite number N such that $\mathfrak{R}(\theta+N)>0$. We can write down a modified integral which shall express all but the first N terms of $S(s)$. The argument used above will hold for the modified integral; the proposition to be proved is evidently true for the first N terms of $S(s)$. And therefore we may establish that the theorem is true under the sole limitation $\mathfrak{R}(\beta+s)>0$, θ not being zero or a negative integer.

§ 27. We will next show that, *if* C_1 *be a contour in the finite part of the plane parallel to the imaginary axis and cutting the real axis in a point for which* $\mathfrak{R}(s)>-\mathfrak{R}(\beta)$, *and if* $\mathfrak{R}(x)>0$, $e^{-x}G_\beta(x;\theta) = -\frac{1}{2\pi\iota}\int_{C_1} S(s)\,x^s\,ds$.

In the first place we see that this integral is finite. For the series for $S(s)$ is convergent if $\mathfrak{R}(s+\beta)>0$, and as $|v|$ tends to infinity, $|S(s)x^s| < K|x^{\mathfrak{R}(s)}|e^{|v\arg x|-\frac{1}{2}\pi|v|}$. Thus the subject of integration tends exponentially to zero if $|\arg x| < \frac{1}{2}\pi$.

Let now C be a contour embracing the positive half of the real axis and cutting this axis in the same point as C_1. As we are ultimately to make $\mathfrak{R}(\beta)$ very large, we shall assume that C_1 includes the origin.

Evidently by Cauchy's theory of residues

$$-\frac{1}{2\pi\iota}\int_C \Gamma(n-s)\,x^s\,ds = \sum_{m=0}^{\infty}\frac{(-)^m x^{n+m}}{m!} = e^{-x}x^n.$$

Hence if ${}_N G_\beta(x;\theta)$ denote the sum of the first $(N+1)$ terms of the series by which $G_\beta(x;\theta)$ is defined,

$$e^{-x}{}_N G_\beta(x;\theta) = -\frac{1}{2\pi\iota}\int_C \sum_{n=0}^{N}\frac{\Gamma(n-s)}{n!\,(n+\theta)^\beta}\,x^s\,ds.$$

Now, if $|\arg x| < \frac{1}{2}\pi$, $|\Gamma(n-s)\,x^s|$ tends exponentially to zero as n tends to infinity if $\mathfrak{R}(s) >$ a finite negative quantity, and if s be not in the neighbourhood of the poles of $\Gamma(-s)$.

Therefore the previous integral will vanish when taken round an infinite contour for which $\mathfrak{R}(s) >$ a finite negative quantity. Hence

$$e^{-x}G_N(x;\theta) = -\frac{1}{2\pi\iota}\int_{C_1} \sum_{n=0}^{N}\frac{\Gamma(n-s)}{n!\,(n+\theta)^\beta}\,x^s\,ds.$$

Suppose now that N tends to infinity. Each side of the equality tends to a definite finite limit, and we have the given theorem.

§ 28. We will now *show that, if l be a positive quantity such that* $|n+\theta| > l$, $(n = 0, 1, 2, \dots \infty)$, *and if* R *be any finite quantity, however large, such that* $\mathfrak{R}(\beta) > \mathrm{R}+\epsilon$, *where* $\epsilon > 0$, $e^{-x}l^{\beta}\mathrm{G}_{\beta}(x\,;\theta) = \mathrm{J}(x)/x^{\mathrm{R}}$, *where* $|\mathrm{J}(x)|$ *can be made as small as we please, for all values of* $\mathfrak{R}(\beta)$ *however large, by sufficiently increasing* $|x|$.

For we have

$$e^{-x}l^{\beta}\mathrm{G}_{\beta}(x\,;\theta) = -\frac{1}{2\pi\iota}\int_{\mathrm{C}_1}\sum_{n=0}^{\infty}\frac{\Gamma(n-s)\,l^{\beta}}{n!\,(n+\theta)^{\beta}}\,x^{s}\,ds.$$

We take the straight contour to cut the real axis in the point $-\mathrm{R}-\epsilon'$, where $0 < \epsilon' < \epsilon$.

Putting $s = -\mathrm{R}-\epsilon'+\iota v$, the integral becomes

$$x^{-\mathrm{R}-\epsilon'}\frac{1}{2\pi}\int_{\mathrm{C}_1}\sum_{n=0}^{\infty}\frac{\Gamma(n+\mathrm{R}+\epsilon'-\iota v)\,l^{\beta}}{n!\,(n+\theta)^{\beta}}\,x^{\iota v}\,dv = x^{-\mathrm{R}}\mathrm{J}(x) \quad \text{(say)}.$$

From this integral we can show that $|\mathrm{J}(x)|$ can be made as small as we please by taking $|x|$ sufficiently large. And as $|\beta|$ increases indefinitely $|\mathrm{J}(x)|$ can be made as small as we please.

We thus have the theorem enunciated.

It is evident that by studying the singularities of the function $\mathrm{S}(s)$ we could obtain anew the asymptotic expansion of $\mathrm{G}_{\beta}(x\,;\theta)$ when $\mathfrak{R}(x) > 0$. This problem I reserve for a future occasion.

PART IV.

The Singularities of $g_{\beta}(x\,;\theta)$.

§ 29. The function $g_{\beta}(x\,;\theta)$ defined when $|x| < 1$ by series $\sum_{n=0}^{\infty} x^{n}/(n+\theta)^{\beta}$ can be studied by the methods previously developed.

We assume that θ is not zero or a negative integer, and that β is not equal to zero or a positive integer. When $\beta = 1$, the function becomes $g(x\,;\theta)$ previously considered in Part II. When β is a positive integer, the function can be derived from the case $\beta = 1$ by differentiation with regard to θ.

On account of the length of this paper I give some theorems relating to this function, leaving the development of the theory for publication elsewhere.[*]

I. The function $g_{\beta}(x\,;\theta)$ has a single singularity in the finite part of the plane. This singularity occurs at $x = 1$ and is not an essential singularity. Near $x = 1$, $g_{\beta}(x\,;\theta)$ is many-valued.

II. The function $g_{\beta}(x\,;\theta)-g_{\beta}(x\,;1)\,x^{1-\theta}$ has no singularities in the finite part of the plane, except the singularity due to $x^{1-\theta}$ at the origin, and if $|\log x| < 2\pi$, it admits the expansion

$$x^{-\theta}\sum_{n=0}^{\infty}\frac{(\log x)^{n}}{n!}\left\{\zeta(\beta-n,\theta)-\zeta(\beta-n,1)\right\},$$

where $\zeta(s, a)$ is the simple Riemann ζ-function of parameter unity.

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[*] See a forthcoming paper in the 'Proceedings of the London Mathematical Society.'

III. The function $g_\beta(x;\theta) - \Gamma(1-\beta)(-\log x)^{\beta-1}x^{-\theta}$ is one-valued near $x = 1$, and in the vicinity of this point admits the convergent expansion

$$\sum_{n=0}^{\infty} \frac{(x-1)^n}{x^{n+1}} \bar{\zeta}_{n+1}(\beta, \theta),$$

where $\bar{\zeta}_{n+1}(\beta, \theta)$ denotes the $(n+1)$ ple Riemann ζ-function of equal parameters unity.

IV. If θ be not real, the function

$$g_\beta(x;\theta) + g_\beta\left(\frac{1}{x}; -\theta\right) e^{\mp\pi i\beta},$$

the negative or positive sign being taken as $I(\theta)$ is $>$ or < 0, is one-valued near $x = 1$, and has no singularity at this point.

V. If θ be not zero or a positive or negative integer, $g_\beta(x;\theta)$ admits, when $|x|$ is very large, the asymptotic expansion

$$-\sum_{n=1}^{\infty} \frac{1}{x^n(\theta-n)^\beta} + \frac{[\log(-x)]^{\beta-1}}{(-x)^\theta} \sum_{n=0}^{\infty} \frac{(-)^n \left(\dfrac{\pi}{\sin \pi\theta}\right)^{(n)}}{n!\,\Gamma(\beta-n)[\log(-x)]^n}.$$

This theorem is true when β is a positive integer, in which case the final series is a finite series of β terms.

When θ is a positive integer, a modification of the formula can be deduced.

When $\theta = 1$ and β is a positive integer, we obtain SPENCE's formula.*

VI. Similar analysis holds for the more general function defined when $|x| < 1$ by

$$\sum_{n=0}^{\infty} \frac{x^n[\log(n+\theta)]^k}{(n+\theta)^\beta}.$$

PART V.

The Function $F_\beta(x;\theta) = \sum_{n=0}^{\infty} \frac{x^n \chi(n+\theta)}{n!\,(n+\theta)^\beta}$.

§ 30. We proceed now to use the previous asymptotic expansions to obtain similar expansions for very general types of integral functions.

Let $\chi(x)$ be a function of x which outside a circle of radius l admits the expansion $\sum_{r=0}^{\infty} b_r/x^r$, so that for values of r greater than an assignable quantity R, $|b_r| < l'^r$, where $l' > l$.

Suppose further that the points θ, $\theta+1$, $\theta+2\ldots$ all lie outside this circle, and that the modulus of the least of them is taken to be $> l'$.

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* DE MORGAN, 'Differential and Integral Calculus,' 1842, p. 659.

We proceed to show that the function

$$F_\beta(x\,;\,\theta) = \sum_{n=0}^{\infty} \frac{x^n \chi(n+\theta)}{(n+\theta)^\beta\,\Gamma(n+1)}$$

may be written as the sum of functions

$$\sum_{r=0}^{\infty} b_r G_{\beta+r}(x\,;\,\theta),$$

and to obtain its asymptotic expansion when $|\arg x| < \pi/2$.

We have at once

$$F_\beta(x\,;\,\theta) = \sum_{n=0}^{\infty} \frac{x^n}{n\,!}\left[\sum_{r=0}^{k} \frac{b_r}{(n+\theta)^{\beta+r}} + \sum_{r=1}^{\infty} \frac{b_{k+r}}{(n+\theta)^{\beta+k+r}}\right]$$

If then $k > R$, we have

$$\left|\sum_{r=1}^{\infty} \frac{b_{k+r}}{(n+\theta)^{\beta+k+r}}\right| < \sum_{r=1}^{\infty} \frac{l'^{k+r}}{|(n+\theta)^{\beta+k}|\,|(n+\theta)^r|} < \frac{l'^k}{|(n+\theta)^{\beta+k}|}\sum_{r=1}^{\infty}\frac{l'^r}{\mu^r},$$

where μ is the minimum value of $|n+\theta|$.

The modulus of the series is therefore less than

$$\frac{l'^{k+1}}{|(n+\theta)^{\beta+k}|\,(\mu-l')}, \text{ since } \mu > l'.$$

Hence

$$F_\beta(x\,;\,\theta) = \sum_{r=0}^{k} b_r G_{\beta+r}(x\,;\,\theta) + J_k,$$

where

$$|J_k| < \sum_{n=0}^{\infty} \frac{|x|^n}{n\,!}\,\frac{l'^{k+1}}{|(n+\theta)^{\beta+k}|\,(\mu-l')}.$$

Hence $|J_k|$ tends to zero as k tends to infinity, since $|n+\theta| > l'$. We therefore have

$$F_\beta(x\,;\,\theta) = \sum_{r=0}^{\infty} b_r G_{\beta+r}(x\,;\,\theta),$$

the series being absolutely convergent for all finite values of $|x|$.

§ 31. We will next show *that, when* $|\arg x| < \pi/2$,

$$F_\beta(x\,;\,\theta) = \frac{e^x}{x^\beta}\left[\sum_{s=0}^{\sigma} \frac{S_s}{\Gamma(1-\beta-s)\,x^s} + \frac{J_\sigma(x)}{x^\sigma}\right],$$

where $S_s = \sum_{m=0}^{s} b_m\,{}_m c_{s-m}\,\Gamma(1-\beta-m)$ *and* $|J_\sigma(x)|$ *tends to zero as* $|x|$ *tends to infinity. The coefficients* ${}_r c_n$ *are given by the expansion, valid when* $|y| < 1$,

$$\left[\frac{\log(1-y)}{-y}\right]^{\beta+r-1}(1-y)^{\theta-1} = \sum_{n=0}^{\infty} {}_r c_n\,(-y)^n.$$

We have

$$\mathrm{F}_\beta(x;\theta) = \sum_{r=0}^{\mathrm{R}} b_r \mathrm{G}_{\beta+r}(x;\theta) + \sum_{r=\mathrm{R}+1}^{\infty} b_r \mathrm{G}_{\beta+r}(x;\theta).$$

Consider the second series. However large r may be, we may put

$$|e^{-x} b_r \mathrm{G}_{\beta+r}(x;\theta)| = \frac{\epsilon_r}{|x^{\beta+\mathrm{R}}|},$$

where, by § 28, ϵ_r can be made as small as we please by taking $|x|$ sufficiently large.

Hence

$$\left|\sum_{r=\mathrm{R}+1}^{\infty} b_r \mathrm{G}_{\beta+r}(x;\theta)\, e^{-x} x^{\beta+\mathrm{R}}\right| < \sum_{r=1}^{\infty} \epsilon_{\mathrm{R}+r} < \eta,$$

where η can be made as small as we please by taking $|x|$ sufficiently large. For we have only to take $|x|$ so large that the quantities ϵ_r form an absolutely convergent series.

Again, by the asymptotic expansion for $\mathrm{G}_\beta(x;\theta)$, when $|\arg x| < \pi/2$, we have

$$\sum_{r=0}^{\mathrm{R}} b_r \mathrm{G}_{\beta+r}(x;\theta) = \frac{e^x}{x^\beta} \sum_{r=0}^{\mathrm{R}} \frac{b_r}{x^r} \left[\sum_{n=0}^{\mathrm{N}} \frac{{}_r c_n \Gamma(1-\beta-r)}{\Gamma(1-\beta-r-n)\, x^n} + \frac{\mathrm{I}_\mathrm{N}(x)}{x^\mathrm{N}} \right],$$

where the coefficients ${}_r c_n$ are defined as in the enunciation of the present proposition, and where $|\mathrm{I}_\mathrm{N}(x)|$ can be made as small as we please by taking $|x|$ sufficiently large.

We therefore have

$$\sum_{r=0}^{\mathrm{R}} b_r \mathrm{G}_{\beta+r}(x;\theta) = \frac{e^x}{x^\beta} \left[\sum_{s=0}^{\sigma} \frac{1}{x^s} \sum_{m=0}^{s} \frac{b_m\, {}_m c_{s-m} \Gamma(1-\beta-m)}{\Gamma(1-\beta-s)} + \frac{\mathrm{J}_\sigma(x)}{x^\sigma} \right] \quad . \quad . \quad . \quad (\mathrm{A}),$$

where $\sigma \gtreqless \mathrm{N}$ and $|\mathrm{J}_\sigma(x)|$ can be made as small as we please by taking $|x|$ sufficiently large.

If, now, we take $\mathrm{R} > \sigma$ and combine the two results just obtained, we have the proposition stated.

§ 32. The reader will notice the far-reaching generality of the function whose asymptotic expansion has been obtained. He will also notice that we have shown that from the asymptotic expansion of each of a convergent series of functions we have derived an asymptotic expansion for the function represented by the series of functions.

§ 33. *Let us now consider the asymptotic expansion of* $\mathrm{F}_\beta(x;\theta)$ *when* $\mathfrak{R}(x) < 0$.

We have seen that

$$\mathrm{F}_\beta(x;\theta) = \sum_{r=0}^{\infty} b_r \mathrm{G}_{\beta+r}(x;\theta). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Also, when $|\arg(-x)| < \pi/2$, we have the asymptotic equality

$$\mathrm{G}_{\beta+r}(x;\theta) = (-x)^{-\theta} \{\log(-x)\}^{\beta+r+1} \left\{ \sum_{n=0}^{\mathrm{N}} \frac{(-)^n \Gamma^{(n)}(\theta)}{\Gamma(\beta+r-n)\,\Gamma(n+1)\,[\log(-x)]^n} + \frac{{}_r\mathrm{J}_\mathrm{N}(x)}{[\log(-x)]^\mathrm{N}} \right\},$$

where $|{}_r\mathrm{J}_\mathrm{N}(x)|$ tends to zero as $|x|$ tends to infinity.

By the previous investigation this equality is seen to hold good for all values of r, however large.

Let $F_R(x)$ denote the sum of the first $(R+1)$ terms of the series (1). Then, asymptotically,

$$F_R(x) = (-x)^{-\theta}\{\log(-x)\}^{\beta-1}\sum_{r=0}^{R} b_r\{\log(-x)\}^r$$
$$\left\{\sum_{n=0}^{N}\frac{(-)^n\,\Gamma^{(n)}(\theta)}{\Gamma(\beta+r-n)\,\Gamma(n+1)\,\{\log(-x)\}^n}+\frac{{}_rJ_N(x)}{\{\log(-x)\}^N}\right\}.$$

It is at once evident that any attempt to make R tend positively to infinity will introduce a series in ascending powers of $\log(-x)$. This series cannot be asymptotic: it may be convergent, or it may be divergent but summable. In order to investigate its nature, we shall limit ourselves to the case where β is a positive integer. In this case the series proceeding in descending powers of $\log(-x)$ will be finite, and if we take $N = \beta+r-1$, $|{}_rJ_N(x)|$ is less than $1/|x|^l$, when $|x|$ is large, however large l may be.

We have then

$$F_R(x) = (-x)^{-\theta}\{\log(-x)\}^{\beta-1}\sum_{r=0}^{R}\left[\sum_{n=0}^{\beta+r-1}\frac{(-)^n\,\Gamma^{(n)}(\theta)\,b_r}{\Gamma(\beta+r-n)\,\Gamma(n+1)\,\{\log(-x)\}^{n-r}}+b_r\,{}_rJ(x)\right].$$

The double series may be written

$$\left\{\sum_{s=-\beta+1}^{-1}\sum_{r=0}^{R}+\sum_{s=0}^{R}\sum_{r=s}^{R}\right\}\left[\frac{(-)^{r-s}\,\Gamma^{(r-s)}(\theta)\,b_r\{\log(-x)\}^s}{\Gamma(\beta+s)\,\Gamma(r-s+1)}\right].$$

Thus

$$(-x)^{\theta}\{\log(-x)\}^{1-\beta}F_R(x) = \sum_{s=1}^{\beta-1}\frac{[\log(-x)]^{-s}}{\Gamma(\beta-s)}\sum_{r=0}^{R}\frac{(-)^{r+s}\,\Gamma^{(r+s)}(\theta)\,b_r}{\Gamma(r+s+1)}$$
$$+\sum_{s=0}^{R}\frac{\{\log(-x)\}^s}{\Gamma(\beta+s)}\sum_{r=0}^{R-s}\frac{(-)^r\,b_{r+s}\,\Gamma^{(r)}(\theta)}{\Gamma(r+1)}+\sum_{r=0}^{R} b_r\,{}_rJ(x).$$

§ 34. Suppose now that R tends to infinity. The series $\left|\sum_{r=0}^{\infty} b_r\,{}_rJ(x)\right|$ can, even when multiplied by *any* finite positive power of $|x|$, be made as small as we please by taking $|x|$ sufficiently large.

The series $\sum_{r=0}^{\infty}\frac{(-)^r\,b_r\,\Gamma^{(r+s)}(\theta)}{\Gamma(r+s+1)}$ is absolutely convergent. For if μ be the minimum value of $|(n+\theta)|$, so that μ is the distance of θ from the nearest of the points $0, -1, -2, \ldots$, we have, if $|x| < \mu$,

$$\Gamma(x+\theta) = \sum_{m=0}^{\infty}\frac{\Gamma^{(m)}(\theta)}{\Gamma(m+1)}x^m.$$

Therefore

$$\underset{m=\infty}{Lt}\left|\left[\frac{\Gamma^{(m)}(\theta)}{\Gamma(m+1)}\right]^{1/m}\right| = \frac{1}{\mu}.$$

Thus, since $\underset{r=\infty}{Lt}\,|b_r^{1/r}| = l$, the series is absolutely convergent, since $\mu > l$.

Again, where s is sufficiently large, $|b_{r+s}| < l'^{r+s}$, where $l' > l$; and therefore

$$\left| \sum_{r=0}^{\mathrm{R}-s} \frac{(-)^r b_{r+s} \Gamma^{(r)}(\theta)}{\Gamma(r+1)} \right| < \mathrm{K} l'^s,$$

where K is finite and independent of s for all values of R, however large, provided $\mu > l'$.

Hence, when R tends to infinity,

$$\left| \sum_{s=0}^{\mathrm{R}} \frac{\{\log(-x)\}^s}{\Gamma(\beta+s)} \sum_{r=0}^{\mathrm{R}-s} \frac{(-)^r b_{r+s} \Gamma^{(r)}(\theta)}{\Gamma(r+1)} \right| < \mathrm{K} \sum_{s=0}^{\infty} \left| \frac{\{l' \log(-x)\}^s}{\Gamma(\beta+s)} \right| + \mathrm{L},$$

where L is finite; and thus the series is convergent provided $|\log(-x)|$ is finite.

We therefore have the asymptotic equality

$$\mathrm{F}_\beta(x;\theta) = \left\{ \phi\{\log(-x)\} + \sum_{s=1}^{\beta-1} \frac{[\log(-x)]^{-s}}{\Gamma(\beta-s)} \sum_{r=0}^{\infty} \frac{(-)^{r+s} b_r \Gamma^{(r+s)}(\theta)}{\Gamma(r+s+1)} \right.$$
$$\left. + \mathrm{J}(x) \right\} (-x)^{-\theta} \{\log(-x)\}^{\beta-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{B}).$$

This equality is valid provided $\mathfrak{R}(x) < 0$. The function $\mathrm{J}(x)$ is such that its modulus, even when multiplied by $|x|^l$, however large the finite quantity l may be, can be made as small as we please by taking $|x|$ sufficiently large. And $\phi(x)$ denotes the integral function

$$\sum_{s=0}^{\infty} \frac{x^s}{\Gamma(\beta+s)} \sum_{r=0}^{\infty} \frac{(-)^r b_{r+s} \Gamma^{(r)}(\theta)}{\Gamma(r+1)} = \sum_{s=0}^{\infty} \frac{x^s \mathrm{T}_s}{\Gamma(\beta+s)} \text{ (say).}$$

The quantity $\log(-x)$ is such that the modulus of its imaginary part is less than $\pi/2$.

We see then that the process which we have employed, even in the case where β is an integer, makes the asymptotic expansion of $\mathrm{F}_\beta(x;\theta)$, when $\mathfrak{R}(x) < 0$, depend on that of the integral function of $\log(-x)$ which we have written $\phi\{\log(-x)\}$.

§ 35. *We proceed now to apply the theory of contour integration to this problem.*

We have

$$\mathrm{F}_\beta(x;\theta) = \sum_{n=0}^{\infty} \frac{x^n \chi(n+\theta)}{(n+\theta)^\beta \Gamma(n+1)},$$

and $\chi(x)$ admits the expansion $\sum\limits_{n=0}^{\infty} b_n/x^n$ outside a circle of finite radius l.

We may represent $\mathrm{F}_\beta(x;\theta)$ by the contour integral

$$-\frac{1}{2\pi\iota} \int_{\mathrm{L}_0} \frac{(-x)^s \Gamma(-s) \chi(s+\theta)}{(s+\theta)^\beta} ds,$$

taken round a contour L_0 embracing the positive half of the real axis and enclosing $s = 0, 1, 2, \ldots \infty$, but no other poles of the subject of integration. If $l < |\theta+n|$, $n = 0, 1, 2, \ldots \infty$, the whole circle of convergence of $\chi(s+\theta)$, *i.e.*, a circle of radius l and centre $-\theta$, lies outside the contour L_0. If the inequality does not hold, the contour L_0 has to be indented to include $s = 0, 1, 2, \ldots$, but no singularities of $\chi(s+\theta)$. This is always possible if $\chi(\theta+n)$ is not infinite for any positive integral (including zero) value of n.

Suppose now that $|\arg(-x)| < \pi/2$. Then the integral will vanish along any part of an infinite contour for which $\mathfrak{R}(s)$ is greater than a finite negative quanity k (say).

Hence, if $|\arg(-x)| < \frac{\pi}{2}$,

$$F_\beta(x;\theta) = -\frac{1}{2\pi\iota}\int_{L_2} \frac{(-x)^s\Gamma(-s)\chi(s+\theta)}{(s+\theta)^\beta}\,ds,$$

taken along a contour L_2 which consists of the infinite line $s = -k$, and a loop from a point on this line which includes the singularities of $\chi(s+\theta)$, but none of those of $\Gamma(-s)$.

Hence if we neglect terms of order $1/|x|^k$, we see that, when $|x|$ is large and $|\arg(-x)| < \frac{1}{2}\pi$, we have

$$F_\beta(x;\theta) = -\frac{(-x)^{-\theta}}{2\pi\iota}\int (-y)^{-\beta}\chi(-y)\,e^{-y\log(-x)}\,\Gamma(y+\theta)\,dy\,. \quad . \quad . \quad . \quad (1)$$

taken round a contour which encloses within its bulb the singularities of $\chi(-y)$, but none of the points $-\theta$, $-\theta-1$, $-\theta-2, \ldots$, and which embraces the positive half of the real axis. In this integral the principal value of $\log(-x)$, which is real when x is real and negative, must be taken. It is by evaluating this integral for assigned values of $\chi(-y)$ that we can obtain the asymptotic expansion of $F_\beta(x;\theta)$ when $\mathfrak{R}(x) < 0$.

§ 36. Consider the case when β is an integer, positive or negative. In this case the subject of integration is one-valued. The integral can therefore be taken along a finite contour which encloses the singularities of $\chi(y)$, but not the poles of $\Gamma(y+\theta)$. The residues at the latter points will give rise to a finite number of algebraical terms, *i.e.*, terms which involve algebraical powers of x, if there are any such points within the circle of convergence of $\chi(y)$. Making due allowance for such terms, we may take the integral round a circle just larger than this circle of convergence. This integral when $|x|$ is large will be at most of order $|x^{l-\theta}|$. *The same is true of the more general integral* (1) *when β is not an integer.* We thus get a superior limit to the asymptotic value of $F_\beta(x;\theta)$ when $\mathfrak{R}(x) < 0$ and β is or is not integral.

Further progress must be made by a detailed examination of the singularities of $\chi(y)$ within its circle of convergence.

The Function $f(x) = \sum\limits_{n=0}^{\infty} \frac{x^n e^{\frac{1}{n+\theta}}}{\Gamma(n+1)}$.

§ 37. *To illustrate the general theory which has just been developed, we will discuss the function*

$$f(x) = \sum_{n=0}^{\infty} \frac{x^n e^{\frac{1}{n+\theta}}}{\Gamma(n+1)},$$

in which θ is not zero or a negative integer.

With our previous notation we have $\beta = 0$, $b_m = 1/m!$, and l may be taken as small as we please.

Hence, when $\mathfrak{R}(x) > 0$, we have

$$f(x) = e^x \left\{ \sum_{s=0}^{\sigma} \frac{\mathrm{S}_s}{x^s} + \frac{\mathrm{J}_\sigma(x)}{x^\sigma} \right\},$$

where $|\mathrm{J}_\sigma(x)|$ tends to zero as $|x|$ tends to infinity, and where

$$\mathrm{S}_s = \underset{\beta=0}{\mathrm{L}t} \sum_{m=0}^{s} \frac{{}_m c_{s-m} \Gamma(1-\beta-m)}{m!\,\Gamma(1-\beta-s)} = \sum_{m=0}^{s} \frac{(-)^{s-m}{}_m c_{s-m} \Gamma(s)}{m!\,\Gamma(m)}.$$

Now the coefficients ${}_m c_n$ are given by the expansion, valid when $|y| < 1$,

$$\{\log(1-y)/(-y)\}^{m-1} (1-y)^{\theta-1} = \sum_{n=0}^{\infty} {}_m c_n (-y)^n.$$

Hence S_s is the coefficient of $(-y)^{s-1}$ in the expansion of

$$\Gamma(s) \left[\sum_{m=0}^{\infty} \frac{(-)^{s-m} \{\log(1-y)\}^{m-1}}{m!\,(m-1)!} \right] (1-y)^{\theta-1}$$

in ascending powers of y when $|y| < 1$.

The reader will notice the connection between the series in the square brackets and $\mathrm{J}_0\{\log(1-y)\}$, where $\mathrm{J}_0(x)$ is Bessel's function of zero order.

When $\mathfrak{R}(x) > 0$, we have now obtained the asymptotic expansion

$$f(x) = e^x \sum_{s=0}^{\infty} \frac{\mathrm{S}_s}{x^s}.$$

§ 38. *Consider next the case when $\mathfrak{R}(x) < 0$.*

Then, if $|\arg(-x)| < \pi/2$, we see that $f(x)$ is equal to

$$\frac{1}{2\pi\iota} \int (-x)^s \Gamma(-s) e^{\frac{1}{s+\theta}} ds,$$

provided we neglect terms whose modulus when multiplied by $|x|^l$, where l has any finite value, can be made as small as we please by taking $|x|$ sufficiently large. The integral is taken in the positive direction round a small circle enclosing $s = -\theta$.

The integral is equal to

$$(-x)^{-\theta}\sum_{n=0}^{\infty}\frac{[\log(-x)]^n}{n!}\,\mathrm{K}_n,$$

where K_n is the coefficient of $\epsilon^{-(n+1)}$ in the expansion of $\Gamma(\theta-\epsilon)\exp\{1/\epsilon\}$.

We therefore have

$$\mathrm{K}_n = \sum_{m=0}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m\,!\,(m+n+1)\,!}.$$

Hence, when $\mathfrak{R}(x) < 0$,

$$f(x) = (-x)^{-\theta}\sum_{n=0}^{\infty}\frac{[\log(-x)]^n}{n\,!}\sum_{m=0}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m\,!\,(m+n+1)\,!} + \mathrm{J}(x),$$

where $|\mathrm{J}(x)\,x^l|$ for any finite value of l tends to zero as $|x|$ tends to infinity.

The double series obviously represents an integral function of $\log(-x)$, and may be written

$$\sum_{m=0}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m\,!}\sum_{n=0}^{\infty}\frac{y^n}{n\,!\,(m+1+n)\,!},\ \text{where } y = \log(-x).$$

Using the notation ${}_0\mathrm{F}_1\{\rho\,;\,x\}$ for the series

$$\sum_{n=0}^{\infty}\frac{y^n\,\Gamma(\rho)}{n\,!\;\Gamma(\rho+n)},$$

the double series may be written

$$\phi(y) = \sum_{m=0}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m\,!\,(m+1)\,!}\,{}_0\mathrm{F}_1\{m+2\,;\,y\}.\quad \text{(Compare Part X.)}$$

§ 39. *We proceed now to obtain an asymptotic expansion for this integral function of y.*

For this purpose we shall anticipate the asymptotic expansions of the hypergeometric series ${}_0\mathrm{F}_1\{\rho\,;\,y\}$, which will be subsequently developed.

We shall show that asymptotically (§ 51, III.)

$${}_0\mathrm{F}_1\{\rho\,;\,y\} = e^{2\sqrt{y}}\,\frac{\Gamma(2\rho-1)}{\Gamma(\rho-\frac{1}{2})}\{4\sqrt{y}\}^{1/2-\rho}\,{}_2\mathrm{F}_0\left\{\rho-\tfrac{1}{2},\,\tfrac{3}{2}-\rho\,;\,\frac{1}{4\sqrt{y}}\right\},$$

wherein $\mathfrak{R}(y) > 0$ and $\sqrt{y}$ denotes the positive value of the square root when y is real and positive.

The series

$${}_2\mathrm{F}_0\{\rho_1,\,\rho_2\,;\,x\} = 1 + \frac{\rho_1\rho_2}{1}x + \frac{\rho_1(\rho_1+1)(\rho_2)(\rho_2+1)}{1\,.\,2}x^2 + \ldots$$

The modulus of the error which results from stopping at any term of the given series is less than that of the last term retained when $|y|$ is very large.

We shall also show that however large $\mathfrak{R}(\rho)$ may be, if m be any finite quantity $\lesssim \rho$, we may put

$$ {}_0F_1\{\rho\,;\,y\} = e^{2\sqrt{y}}\,\frac{I_\rho(y)}{y^{(m-1)/2}}, $$

where, by taking $|y|$ sufficiently large, we may make $|I_\rho(y)|$ as small as we please; and where $|I_\rho(y)|$ tends to a finite limit as ρ tends to infinity, $|y|$ remaining constant.

We now put

$$ \phi(y) = \left[\sum_{m=0}^{R} + \sum_{m=R+1}^{\infty}\right]\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m\,!\,(m+1)\,!}\,{}_0F_1\{m+2\,;\,y\}. $$

The first series in which the summation is taken from 0 to R is equal to

$$ e^{2\sqrt{y}}\left[\sum_{m=0}^{R}\frac{(-)^m\Gamma^{(m)}(\theta)}{m!\,(m+1)!}\,\frac{\Gamma(2m+3)}{\Gamma(m+3/2)}\,[4\sqrt{y}]^{-m-3/2}\cdot{}^{R-m+1}_{\;\;2}F_0\left\{m+3/2,\,-1/2-m\,;\,\frac{1}{4\sqrt{y}}\right\}+\frac{J_1(y)}{y^{R/2+3/4}}\right], $$

where ${}^{k}_{2}F_0\{y\}$ denotes that the sum of the first k terms of the series in ascending powers of y is to be taken. The modulus of $J_1(y)$ can be made as small as we please by taking $|y|$ sufficiently large.

The second series

$$ \sum_{m=R+1}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m!\,(m+1)!}\,{}_0F_1\{m+2\,;\,y\} $$

is equal to

$$ e^{2\sqrt{y}}\sum_{m=R+1}^{\infty}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m!\,(m+1)!}\,\frac{I_m(y)}{y^{(R+2)/2}}, $$

where $|I_m(y)|$ for all values of m can be made as small as we please by sufficiently increasing $|y|$.

Since $\sum\limits_{m=0}^{\infty}\dfrac{(-)^m\,\Gamma^{(m)}(\theta)}{m!\,(m+1)!}$ is absolutely convergent, we see that the second series may be written

$$ e^{2\sqrt{y}}\,\frac{J_2(y)}{y^{(R+2)/2}}, $$

when $|J_2(y)|$ tends to zero as $|y|$ tends to infinity.

Finally, therefore, if $\mathfrak{R}(x) < 0$ and $|\arg(-x)| < \pi/2$, $f(x)$ admits the asymptotic equality

$$ (-x)^{-\theta}\exp\{2\sqrt{\log(-x)}\}\,\{4\sqrt{\log(-x)}\}^{-3/2}\left[\sum_{m=0}^{R}\frac{(-)^m\,\Gamma^{(m)}(\theta)}{m!\,(m+1)!}\,\frac{(2m+2)!}{\Gamma(m+3/2)}\,[4\sqrt{\log(-x)}]^{-m}\right. $$
$$ \left.{}^{R-m+1}_{\;\;2}F_0\left\{m+3/2\,,\,-\tfrac{1}{2}-m\,;\,\frac{1}{4\sqrt{\log(-x)}}\right\}+\frac{J(x)}{\{\log(-x)\}^{R/2}}\right], $$

where $|J(x)|$ can be made as small as we please by taking $|x|$ sufficiently large.

§ 40. We have therefore obtained the nature of the asymptotic expansion of $f(x)$ for the two cases when $\mathfrak{R}(x) > 0$ and when $\mathfrak{R}(x) < 0$.

The integral which was employed in § 35 showed us that in the latter case $|f(x)|$ when $|x|$ is very large is of order less than the order of $|(-x)^{-\theta}|\,|x^{\epsilon}|$ when $\epsilon > 0$.

We readily see that this is in agreement with the preceding result.

The investigation just concluded has emphasised the fact that the asymptotic expansion of the more general function considered at the beginning of this Part of the memoir demands, when $\mathfrak{R}(x) < 0$, a knowledge of the nature of the finite singularities of $\chi(x)$.

Part VI.

The Function $f_\beta(x;\theta) = \sum_{n=0}^{\infty} \frac{x^n\chi(n+\theta)}{(n+\theta)^\beta}$, *when* $|x| < 1$.

§ 41. The function $f_\beta(x;\theta)$ is defined when $|x| < 1$ by the series $\sum_{n=0}^{\infty} \frac{x^n\chi(n+\theta)}{(n+\theta)^\beta}$, where outside a circle of radius $l < \mu$, where μ is the least of the quantities $|n+\theta|$, $n = 0, 1, 2, \ldots \infty$, $\chi(x)$ admits the absolutely convergent expansion $\sum_{r=0}^{\infty} b_r/x^r$.

The following propositions may be established:—

I. When $|x| < 1$, $f_\beta(x;\theta)$ can be written in the form

$$\sum_{r=0}^{\infty} b_r g_{\beta+r}(x;\theta).$$

II. The function $f_\beta(x;\theta)$ has a single singularity in the finite part of the plane. This singularity occurs at $x = 1$, and is a multiform point.

III. Near $x = 1$, $f_\beta(x;\theta)$ behaves like

$$\frac{\pi}{\sin\pi\beta}(-\log x)^{\beta-1}x^{-\theta}\sum_{r=0}^{\infty}\frac{b_r(\log x)^r}{\Gamma(\beta+r)},$$

if β be not a positive or negative integer (zero included). In fact, the difference between $f_\beta(x;\theta)$ and this expression can, when $\mathfrak{R}(x) > 1/2$, be expanded in the absolutely convergent series

$$\sum_{r=0}^{\infty} b_r \sum_{n=0}^{\infty}\frac{(x-1)^n}{x^{n+1}}\bar{\zeta}_{n+1}(\beta+r, \theta).$$

This theorem I first prove for the case when $\mathfrak{R}(\theta) > l' > l$, by means of contour integrals similar to those employed throughout this memoir, and then extend to all values of θ such that $\mu > l$, by means of the difference formulæ for multiple Riemann $\bar{\zeta}$ functions.

IV. Whether β be integral or not, in fact, for all values of β of finite modulus, provided the points $\theta \pm n$, $n = 0, 1, 2, \ldots \infty$ all lie outside the circle of convergence of $\chi(x)$,

$$f_\beta(x;\theta) = -\sum_{n=1}^{\infty}\frac{\chi(\theta-n)}{x^n(\theta-n)^\beta} - \frac{1}{2\pi\iota}\int_{C'}\frac{\pi(-x)^{-\theta-y}\chi(-y)\,dy}{\sin\pi(\theta+y)(-y)^\beta},$$

where C′ is a contour which embraces the positive half of the real axis and includes within its bulb the circle of convergence of $\chi(y)$.

V. When $|x|$ is very large, the final integral in the equality just written is equal to $(-x)^{l'-\theta}\,\mathrm{J}(x)$, where, if $l' > l$, $|\mathrm{J}(x)|$ tends to zero as $|x|$ tends to infinity. We thus obtain a superior limit to the asymptotic value of $f_\beta(x;\theta)$ when $|x|$ is large. The problem of actually obtaining an asymptotic expansion depends upon a knowledge of the singularities of $\chi(y)$ within its circle of convergence.

PART VII.

The Functions $\sum_{n=0}^{\infty} \frac{x^n\Gamma(1+\alpha n)}{\Gamma(1+n)}\ (0 \gtreqless \alpha < 1)$ *and* $\sum_{n=0}^{\infty} \frac{x^n\Gamma(1+n\theta)}{\Gamma(1+n+n\theta)}\ (\theta > 0)$.

§ 42. The asymptotic expansions of these two functions are connected with one another. The functions do not belong to the categories previously considered; their *associated* functions have not finite radius of convergence.

We give the results which may be obtained for these two functions, referring the reader elsewhere for the detailed analysis.*

I. If

$$f(x) = \sum_{n=0}^{\infty} \frac{x^n\Gamma(1+\alpha n)}{\Gamma(n+1)},\ \text{we have, if } \alpha < 1,\ f(x) = \int_0^{\infty} \exp\{-y+xy^{\alpha}\}\,dy,$$

the integration being taken along the positive half of the real axis.

Hence, if $\mathfrak{R}(x) < 0$, we have the asymptotic expansion

$$f(x) = \frac{1}{\alpha(-x)^{1/\alpha}} \sum_{n=0}^{\infty} \frac{(-)^n\Gamma((n+1)/\alpha)}{\Gamma(n+1)(-x)^{n/\alpha}},$$

the principal value of $(-x)^{1/\alpha}$, which is real when x is real and negative, and which has a cross-cut along the positive half of the real axis, being taken.

II. When $\mathfrak{R}(x) > 0$ and $|\arg x| < (1-\alpha)\frac{1}{2}\pi$, we have

$$f(x) = (\alpha x)^{\frac{1}{1-\alpha}} \int_0^{\infty} \exp\{(\alpha^{\alpha}x)^{\frac{1}{1-\alpha}}(t^{\alpha}-\alpha t)\}\,dt.$$

By the substitution $y = \frac{1}{\alpha} - 1 - \frac{t^{\alpha}}{\alpha} + t$ we deduce the asymptotic expansion

$$f(x) = \exp\{(1-\alpha)\,\alpha^{\frac{\alpha}{1-\alpha}}x^{\frac{1}{1-\alpha}}\}\,(\alpha x)^{\frac{1}{2(1-\alpha)}}\left(\frac{2}{1-\alpha}\right)^{1/2}\left[\Gamma(\tfrac{1}{2}) + \sum_{n=1}^{\infty} \frac{c_n}{(\alpha x)^{\frac{n}{(1-\alpha)}}}\right],$$

the c_n's being definite constants.

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* See a paper which will shortly appear in 'Cambridge Philosophical Transactions,' vol. 20.

III. When $\frac{\pi}{2} \geqq |\arg x| > \frac{1}{2}(1-\alpha)\pi$, we may obtain the same expansion as in Case I.

IV. The expansions of Cases I. and III. may also be obtained by considering the contour integral

$$-\frac{1}{2\pi\iota}\int \Gamma(-s)(-x)^s \Gamma(\alpha s+1)\, ds.$$

V. When $\alpha = 1/2$, we obtain the asymptotic expansion

$$f(x) = \mathrm{P}e^{\frac{1}{4}x^2} x\Gamma\left(\tfrac{1}{2}\right) + \frac{2}{x^2}\sum_{n=0}^{\infty} \frac{(-)^n \Gamma(2n+2)}{\Gamma(n+1)\, x^{2n}},$$

valid for all values of arg x, if $\mathrm{P} = 0$ when $|\arg x| > \pi/4$.

VI. If $\phi(x)$ denote the function $\sum_{n=1}^{\infty} \frac{x^n \Gamma(1+n\theta)}{\Gamma(1+n+n\theta)}$, $\theta > 0$, we have

$$\phi(x) = \int_0^1 xy^\theta \exp\{xy^\theta(1-y)\}\, dy.$$

Hence, if $\mathfrak{R}(x) > 0$,

$$\phi(x) = \exp\{x\theta^\theta/(\theta+1)^{\theta+1}\}\sqrt{2}\{\theta^{(\theta+1)/2}x^{1/2}/(\theta+1)^{(\theta+2)/2}\} \times \left\{\Gamma\left(\tfrac{1}{2}\right) + \sum_{n=1}^{\infty}\frac{d_n}{x^n}\right\},$$

the d_n's being definite constants.

VII. We can deduce this result from the result of I. by means of the contour integral $-\frac{1}{2\pi\iota}\int \frac{\Gamma(-s)\, x^s \pi\, ds}{\Gamma(-\alpha s)\sin\pi(1-\alpha)s}$.

VIII. By considering the contour integral $\frac{1}{2\pi\iota}\int \frac{x^s \Gamma(1+\theta s)}{\Gamma(1+s+\theta s)} \frac{\pi}{\sin \pi s} ds$, we can show that, when $|\arg x| < \pi/2$,

$$\phi(-x) = -1 - \sum_{n=1}^{\infty} \frac{x^{-n}\Gamma(n+n\theta)}{\Gamma(\theta n)} - \frac{1}{\theta}\sum_{n=0}^{\infty} x^{-(n+1)/\theta}\frac{\Gamma(1+n+(n+1)/\theta)}{\Gamma(1+n)}.$$

Thus, when $\mathfrak{R}(x) < 0$, $\phi(x)$ needs two asymptotic series for its expression.

IX. The previous result can also be obtained by combining the results of III. and VII.

X. Similar analysis can be applied to series of the type

$$\sum_{n=0}^{\infty} \frac{\Gamma(1-n+q\theta n)}{\Gamma(1+\theta n)} x^n,$$

where $\theta > 0$, and q is an integer.

PART VIII.

The Function $E_\alpha(x) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(1+\alpha n)}$, $\alpha > 0$.

§ 43. After the previous investigations it is natural to consider the function $\sum_{n=0}^{\infty} \frac{x^n}{\Gamma(1+\alpha n)}$. This function has been denoted by $E_\alpha(x)$ by MITTAG-LEFFLER,[*] who has discussed its asymptotic behaviour. A reference to his papers will show how differently the methods of this memoir lead us to attack the problem which he has solved.

We will first consider the results which MITTAG-LEFFLER has obtained for the case $0 < \alpha < 2$. He shows that

1. $|E_\alpha(x)|$ approaches zero when $2\pi - \frac{1}{2}\alpha\pi > \phi > \frac{1}{2}\alpha\pi$, where $\arg x = \phi$.
2. When $\phi = \pm\frac{1}{2}\alpha\pi$, $|E_\alpha(x)|$ approaches $\frac{1}{\alpha}$.
3. $\left| E_\alpha(x) - \frac{1}{\alpha}\exp\left[r^{\frac{1}{\alpha}} \cos\frac{\phi}{\alpha}\right]\right|$ diminishes indefinitely when $\frac{1}{2}\alpha\pi > \phi > -\frac{1}{2}\alpha\pi$.

It is evident that, where $\alpha = 0$, $E_\alpha(x) = 1/(1-x)$, and that, when $\alpha < 0$, $E_\alpha(x)$ is an asymptotic series. We assume then $\alpha > 0$.

It is evident that we may write

$$E_\alpha(-x) = \frac{1}{2\pi\iota}\int \frac{\pi x^s}{\Gamma(\alpha s + 1)\sin s\pi}\, ds,$$

where the integral is taken along a contour which encloses the points $s = 0, 1, 2 \ldots \infty$, but no other poles of the subject of integration and which embraces the positive half of the real axis.

Now when $s = u + \iota v$ and $|v|$ is large, $\Gamma(s)$ behaves like $\exp\{-\frac{1}{2}\pi|v|\}$. Therefore the integral vanishes when taken along any part of an infinite contour for which $\mathfrak{R}(s) > -k$, where k is a finite positive quantity, if $|\arg x| < \frac{1}{2}\pi(2-\alpha)$. In order that this equality may have a meaning, we assume $0 < \alpha < 2$.

Hence, under these restrictions,

$$E_\alpha(-x) = \sum_{n=1}^{k} \frac{(-)^{n-1} x^{-n}}{\Gamma(1-\alpha n)} + J_k,$$

where $|J_k|$ is of order less than $\frac{1}{|x|^k}$ when $|x|$ is large.

Changing x into $-x$, we see that, if $0 < \alpha < 2$, we have the asymptotic equality

$$E_\alpha(x) = -\sum_{n=1}^{\infty} \frac{1}{x^n \Gamma(1-\alpha n)} \quad \ldots\ldots\ldots \quad \text{(A)},$$

when $2\pi - \frac{1}{2}\alpha\pi > \arg x > \frac{1}{2}\alpha\pi$.

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[*] MITTAG-LEFFLER, 'Comptes Rendus,' tome 137, pp. 554–558, 1903.

§ 44. *We consider next the asymptotic expansion of* $E_\alpha(x)$ *for other values of arg* x.

For this purpose we investigate the contour integral

$$\frac{1}{2\pi\iota}\int \Gamma(-\alpha s)\frac{\sin\pi(1-\alpha)s}{\sin\pi s}x^s\,ds,$$

which is taken along a contour which embraces the positive half of the real axis and encloses the poles of $\Gamma(-\alpha s)$ and the points $s = 0, 1, 2, \ldots \infty$, but no other poles of the subject of integration.

It is equal to

$$\sum_{m=0}^{\infty}\frac{(-)^{m-1}x^{\frac{m}{\alpha}}}{\alpha m\,!}\frac{\sin\pi\left(\dfrac{1-\alpha}{\alpha}\right)m}{\sin\pi\dfrac{m}{\alpha}}+\sum_{n=0}^{\infty}\frac{(-)^n\Gamma(-\alpha n)\sin\{\pi(1-\alpha)n\}x^n}{\pi}=-\frac{1}{\alpha}\exp\left[x^{\frac{1}{\alpha}}\right]+E_\alpha(x).$$

Now when $s = u+\iota v$ and $|v|$ is very large, the subject of integration tends exponentially to zero if

$$-\tfrac{1}{2}\alpha\pi+\pi|1-\alpha|-\pi+|\arg x|<0.$$

If $\alpha<1$, this condition gives $|\arg x|<\tfrac{3}{2}\pi\alpha$; and if $\alpha>1$, we must have $|\arg x|<2\pi-\tfrac{1}{2}\alpha\pi$.

If these conditions are satisfied, the integral vanishes round that part of the circle at infinity for which $u>-k$, where k is a finite positive quantity.

We may deform the contour in the usual way, and we see that the integral is equal to

$$\sum_{n=1}^{k}\frac{(-)^n\Gamma(\alpha n)\sin\pi(1-\alpha)n}{\pi x^n}+J_k,$$

where J_k denotes the integral along a line parallel to the imaginary axis cutting the real axis between $s=-k$ and $s=-(k+1)$. Thus, when $|x|$ is large, $|J_k|$ is of order less than $1/|x|^k$.

Under the assigned conditions, we therefore have the asymptotic equality

$$E_\alpha(x)-\frac{1}{\alpha}\exp\left[x^{\frac{1}{\alpha}}\right]=-\sum_{n=1}^{\infty}\frac{1}{x^n\,\Gamma(1-\alpha n)}\quad\ldots\ldots\quad(B),$$

in which we have at most neglected terms of order lower than any algebraical power $1/|x|$, when $|x|$ is large.

The conditions show that, when $2>\alpha\geqq 1$, the expansion is valid over the whole plane at infinity. When $1>\alpha>0$ we see that the expansion is valid over all the area at infinity not covered by the condition $2\pi-\tfrac{1}{2}\alpha\pi>\arg x>\tfrac{1}{2}\alpha\pi$ of the previous paragraph as well as over part of that area.

In the investigation of the present paragraph we may have $4>\alpha>2$. If $\alpha = 2+k$, where $k<2$, the asymptotic expansion (B) has only been proved to be valid over the area given by $|\arg x| < \pi - \frac{1}{2}k\pi$.

§ 45. It is at once evident from the expansion (B) that, if $2>\alpha>0$, we have, when $|\arg x| = \frac{1}{2}\alpha\pi$,

$$\mathrm{E}_{\alpha}(x) = \frac{1}{\alpha} \exp\{\pm \iota r^{\frac{1}{\alpha}}\} - \sum_{n=1}^{k} \frac{1}{x^n \Gamma(1-\alpha n)} + \mathrm{J}_k,$$

when $|x| = r$.

Therefore $|\mathrm{E}_{\alpha}(x)|$ behaves like $\frac{1}{\alpha}$.

In thus finding the complete asymptotic expansions for $\mathrm{E}_{\alpha}(x)$, when $0<\alpha<2$, we have incidentally verified all MITTAG-LEFFLER'S results.

§ 46. *We proceed next to consider the asymptotic value of* $\mathrm{E}_{\alpha}(x)$ *when* $\alpha \geqq 2$.

In this case MITTAG-LEFFLER shows that :—

1. If $-\pi < \arg x < \pi$,

$$\left| \mathrm{E}_{\alpha}(x) - \sum_{\mu} \frac{1}{\alpha} \exp\{|x|^{1/\alpha} e^{\iota \frac{2\mu\pi + \arg x}{\alpha}}\} \right|$$

diminishes indefinitely as $|x|$ increases, the summation embracing all real numbers μ, such that

$$\frac{2\mu\pi + \arg x}{\alpha} \leqq \tfrac{1}{2}\pi.$$

2. If $\arg x = \pm\pi$,

$$\left| \mathrm{E}_{\alpha}(x) - \sum_{p=0}^{m-1} \frac{2}{\alpha} \exp\left\{ |x|^{1/\alpha} \cos \frac{2p+1}{\alpha}\pi \right\} \cos\left(|x|^{1/\alpha} \sin \frac{2p+1}{\alpha}\pi \right) \right|$$

(wherein $\alpha = 2m + \vartheta$, $0 \geqq \vartheta \geqq -1$ and $m = 1, 2, 3, \ldots$) diminishes indefinitely as $|x|$ increases.

§ 47. To obtain the complete asymptotic expansions which correspond to these results, we consider the contour integral

$$\frac{1}{2\pi\iota} \int \Gamma(-\alpha s) \frac{\sin \pi (q-\alpha) s}{\sin \pi s} x^s ds,$$

wherein q is an odd positive integer equal to $2p+1$ (say), and the contour of the integral embraces the positive half of the real axis, and encloses the poles of $\Gamma(-\alpha s)$ and the points $s = 0, 1, 2, \ldots \infty$, but no other poles of the subject of integration.

By CAUCHY'S Theorem of Residues the integral is equal to

$$\sum_{m=0}^{\infty} \frac{(-)^{m-1} x^{m/\alpha}}{\alpha m\,!} \cdot \frac{\sin \pi (qm/\alpha - m)}{\sin \pi m/\alpha} + \sum_{m=0}^{\infty} \frac{(-)^m \Gamma(-\alpha m) \sin \pi (q-\alpha) m x^m}{\pi}$$

$$= - \sum_{m=0}^{\infty} \frac{x^{m/\alpha}}{\alpha m!} \frac{\sin \pi q m/\alpha}{\sin \pi m/\alpha} + \sum_{m=0}^{\infty} \frac{x^m}{\Gamma(1+\alpha m)}.$$

Now, if $q = 2p+1$, we have

$$\frac{\sin \pi q m/\alpha}{\sin \pi m/\alpha} = e^{\pi\iota(q-1)m/\alpha} \cdot \frac{1-e^{-2\pi\iota q m/\alpha}}{1-e^{-2\pi\iota m/\alpha}}$$
$$= \sum_{\mu=-p}^{p} e^{2\pi\iota\mu m/\alpha}.$$

Hence the integral is equal to

$$\mathrm{E}_\alpha(x)-(1/\alpha)\sum_{\mu=-p}^{p} \exp\{x^{1/\alpha}e^{2\pi\iota\mu/\alpha}\}.$$

Now, if $s = u+\iota v$, the integral will tend exponentially to zero when $|v|$ is large if

$$-\tfrac{1}{2}\alpha\pi+|2p+1-\alpha|\pi-\pi+|\arg x|<0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

We suppose in the integral that $x^s = \exp\{s \log x\}$, and we take that value of $\arg x$ which is such that $|\arg x| \leqq \pi$.

If now $\alpha > 2p+1$, we obtain from the condition (1)

$$\tfrac{1}{2}\alpha\pi-2(p+1)\pi+|\arg x|<0,$$

and this will hold for all values of $|\arg x|$ which are $\leqq \pi$, provided $\tfrac{1}{2}\alpha < 2p+1$.

On the other hand, if $\alpha<2p+1$, we must have

$$2p\pi-\tfrac{3}{2}\pi\alpha+|\arg x|<0,$$

and this will hold for all values of $|\arg x|$ which are $\leqq \pi$ if $2p+1<\tfrac{3}{2}\alpha$.

The contour integral will therefore vanish, when taken around that part of the circle at infinity bounded by $s=-k$, when k is a finite positive quantity, for all values of $|\arg x|$ which are $\leqq \pi$ if we take p such that either

$$\tfrac{1}{2}\alpha<2p+1<\alpha,$$

or

$$\alpha<2p+1<\tfrac{3}{2}\alpha.$$

In either case therefore the integral will be equal to

$$-\sum_{m=1}^{k} \frac{\Gamma(\alpha m)(-)^m \sin \pi(\alpha-q)m}{\pi x^m}+\mathrm{J}_k,$$

where, when $|x|$ is large, $|\mathrm{J}_k|$ is of lower order than $1/|x|^k$.

We therefore have

$$\mathrm{E}_\alpha(x)-\sum_{\mu=-p}^{p}\frac{1}{\alpha}\exp\{x^{1/\alpha}e^{2\pi\iota\mu/\alpha}\} = -\sum_{m=1}^{k}\frac{1}{\Gamma(1-\alpha m)x^m}+\mathrm{J}_k \quad . \quad . \quad . \quad (\mathrm{C}).$$

This asymptotic equality is valid for all values of $\arg x$ between $\pm\pi$ (the limits included) if p be so chosen that either

$$\frac{\alpha}{2}<2p+1<\alpha,$$

or

$$\alpha<2p+1<\tfrac{3}{2}\alpha.$$

Apparently, then, the expansion is not unique. But this indeterminateness is illusory, for it only corresponds to terms of the sum

$$\sum_{\mu=-p}^{p} \exp\{x^{1/\alpha} e^{2\pi\iota\mu/\alpha}\},$$

for which $\{2\pi\mu + \arg x\}/\alpha$ does not lie between $\pm\frac{1}{2}\pi$.

If we neglect these terms, which may be absorbed in J_k, we may say that $E_\alpha(x)$ admits the asymptotic expansion

$$\frac{1}{\alpha} \sum_{\mu} \exp\{x^{1/\alpha} e^{2\pi\iota\mu/\alpha}\} - \sum_{m=1}^{\infty} \frac{1}{\Gamma(1-\alpha m)\, x^m},$$

wherein μ takes all integral values (positive, negative, or zero) such that

$$2\pi\mu + \arg x \leqq \tfrac{1}{2}\alpha\pi,$$

$\arg x$ having any value between $\pm\pi$, these limits included.

This is equivalent to MITTAG-LEFFLER'S results.

The Function $E_\alpha(x\,;\,\theta, \beta) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(1+\alpha n)(\theta+n)^\beta}$.

§ 48. It is evident that the results just obtained admit of many extensions. As typical of these we may consider the function

$$E_\alpha(x\,;\,\theta, \beta) = \sum_{n=0}^{\infty} \frac{x^n}{\Gamma(1+\alpha n)(\theta+n)^\beta},$$

wherein $\alpha > 0$ and θ is not equal to zero or a negative integer.

We see at once that

$$E_\alpha(-x\,;\,\theta, \beta) = \frac{1}{2\pi\iota} \int \frac{\pi x^s}{\Gamma(\alpha s+1) \sin \pi s\, (s+\theta)^\beta}\, ds,$$

the integral being taken round a contour which embraces the positive half of the real axis and includes the points $s = 0, 1, 2, \ldots \infty$, but no other poles of the subject of integration.

We assume that $x^s = \exp\{s \log x\}$, and that the logarithm has its principal value whose argument lies between $\pm\pi$. We also assume that $(s+\theta)^\beta = \exp\{\beta \log(s+\theta)\}$, and that if θ be not real, the logarithm has its principal value with respect to a cross-cut drawn from $s = -\theta$, parallel to the negative direction of the real axis. If θ were real, we should slightly deform this cross-cut. We omit the consideration of this particular case in the following investigation.

We assume in the first place that $2 > \alpha > 0$. Then if $|\arg x| < \pi(1-\frac{1}{2}\alpha)$, the integral vanishes along that part of a great circle at infinity for which $\mathfrak{R}(s) > -k$.

We therefore have

$$\mathrm{E}_{\alpha}(-x\,;\,\theta,\,\beta) = -\sum_{n=1}^{\infty}\frac{(-)^n x^{-n}}{\Gamma(1-\alpha n)(\theta-n)^{\beta}} - \frac{1}{2\pi\iota}\int\frac{x^{-y-\theta}(-y)^{-\beta}\pi\,dy}{\Gamma(1-\alpha\theta-\alpha y)\sin\pi(\theta+y)},$$

the latter integral embracing the positive half of the real axis and including the origin, but no other singularity of the subject of integration. Since the zeros of $\Gamma(1-\alpha\theta-\alpha y)\sin\pi(\theta+y)$ lie outside the contour, we may employ the summable-divergent series

$$\pi/\{\Gamma(1-\alpha\theta-\alpha y)\sin\pi(\theta+y)\} = \sum_{n=0}^{\infty}(-)^n d_n y^n$$

under the sign of integration. The integral will then be represented asymptotically by

$$-\frac{x^{-\theta}}{2\pi\iota}\sum_{n=0}^{\infty}\int(-y)^{-\beta+n}d_n e^{-y\log x}\,dy = -x^{-\theta}\sum_{n=0}^{\infty}\frac{d_n}{\Gamma(\beta-n)(\log x)^{n-\beta+1}}.$$

If then $|\arg x| < \pi(1-\alpha/2)$, we have the asymptotic expansion

$$\mathrm{E}_{\alpha}(-x\,;\,\theta,\,\beta) = -\sum_{n=1}^{\infty}\frac{1}{\Gamma(1-\alpha n)(\theta-n)^{\beta}(-x)^n} + x^{-\theta}(\log x)^{\beta-1}\sum_{n=0}^{\infty}\frac{d_n}{\Gamma(\beta-n)(\log x)^n}.$$

Therefore when $0 < \alpha < 2$, and $2\pi - \frac{1}{2}\alpha\pi > \arg x > \frac{1}{2}\alpha\pi$, we have

$$\mathrm{E}_{\alpha}(x;\,\theta,\,\beta) = -\sum_{n=1}^{\infty}\frac{1}{x^n\Gamma(1-\alpha n)(\theta-n)^{\beta}} + (-x)^{-\theta}\{\log(-x)\}^{\beta-1}\sum_{n=0}^{\infty}\frac{d_n}{\Gamma(\beta-n)[\log(-x)]^n} \quad (\mathrm{A}).$$

In this formula the principal value of $\log(-x)$, whose imaginary part lies between $\pm\pi$, is to be taken, and $(\theta-n)^{\beta}$ is defined with reference to the cross-cut previously taken.

§ 49. To obtain the asymptotic expansion of $\mathrm{E}_{\alpha}(x\,;\,\theta,\,\beta)$ for other values of $|\arg x|$ when $0 < \alpha < 2$, and for all values of $\arg x$ when $\alpha > 2$, we consider the contour integral

$$\frac{1}{2\pi\iota}\int\Gamma(-\alpha s)\frac{\sin\{\pi(q-\alpha)s\}\,x^s}{\sin\pi s\,(\theta+s)^{\beta}}\,ds$$

round a contour which embraces the positive half of the real axis and includes the poles of $\Gamma(-\alpha s)$ and the points $s = 0, 1, 2, \ldots \infty$, but no other singularities of the subject of integration.

In the subject of integration q is an odd positive integer equal to $2p+1$ (say), and x^s and $(\theta+s)^{\beta}$ are defined as in the previous section. The integral is evidently equal to

$$-\frac{1}{\alpha}\sum_{m=0}^{\infty}\frac{x^{m/\alpha}}{m!}\frac{\sin\pi qm/\alpha}{\sin\pi m/\alpha\,(\theta+m/\alpha)^{\beta}} + \sum_{m=0}^{\infty}\frac{x^m}{\Gamma(1+\alpha m)(\theta+m)^{\beta}}.$$

The first series is equal to

$$-\frac{1}{\alpha}\sum_{\mu=-p}^{p}\sum_{m=0}^{\infty}\frac{x^{m/\alpha}e^{2\pi\iota m\mu/\alpha}}{m!\,(\theta+m/\alpha)^{\beta}} = -\alpha^{\beta-1}\sum_{\mu=-p}^{p}\mathrm{G}_{\beta}\{x^{1/\alpha}e^{2\pi\iota\mu/\alpha}\,;\,\alpha\theta\},$$

where

$$G_\beta(x\,;\theta) = \sum_{m=0}^{\infty} \frac{x^m}{m!\,(m+\theta)^\beta}.$$

Now we have obtained the asymptotic expansion (§ 22)

$$G_\beta(x\,;\theta) = \frac{e^x}{x^\beta} \sum_{n=0}^{\infty} \frac{c_n \Gamma(1-\beta)}{x^n \Gamma(1-\beta-n)} + (-x)^{-\theta} [\log(-x)]^{\beta-1} \sum_{n=0}^{\infty} \frac{(-)^n \Gamma^{(n)}(\theta)}{n!\,\Gamma(\beta-n)\,[\log(-x)]^n},$$

where the c's are defined by the expansion, valid when $y < 1$,

$$\left[\frac{\log(1-y)}{-y}\right]^{\beta-1} (1-y)^{\theta-1} = \sum_{n=0}^{\infty} c_n (-y)^n.$$

If $|\arg x| \leqq \pi$, we see, as before, that it is sufficient to take p such that $\frac{1}{2}\alpha < 2p+1 < \alpha$, or $\alpha < 2p+1 < \frac{3}{2}\alpha$, in order that the integral may vanish for an infinite contour for which $\mathfrak{R}(s) > -k$.

When $1 < \alpha < 2$, we may take $p = 0$. And when $0 < \alpha \leqq 1$, we may take $p = 0$, provided $|\arg x| < \frac{3}{2}\alpha\pi$.

Under these conditions the integral is asymptotically equal to

$$-\sum_{m=1}^{\infty} \frac{1}{\Gamma(1-\alpha m)\,(\theta-m)^\beta\, x^m} - \frac{x^{-\theta}}{2\pi\iota} \int x^{-y} (-y)^{-\beta} \frac{\Gamma(\alpha\theta+\alpha y) \sin\{\pi(\alpha-q)(y+\theta)\}}{\sin\pi(\theta+y)}\, dy.$$

The contour of the integral embraces the positive half of the real axis and contains no singularities of the subject of integration except the origin. The terms neglected in the equality are of order less than any algebraical power of $1/|x|$, when $|x|$ is large.

To obtain an asymptotic expansion for the integral, we may, under the integral sign, employ the summable divergent expansion

$$\frac{\Gamma(\alpha\theta+\alpha y) \sin\{\pi(\alpha-q)(y+\theta)\}}{\sin\pi(\theta+y)} = \sum_{n=0}^{\infty} e_n (-y)^n.$$

The integral is then represented by $x^{-\theta} \sum_{n=0}^{\infty} \frac{e_n}{\Gamma(\beta-n)\,[\log x]^{n-\beta+1}}$.

All these asymptotic expansions are negligible compared with the dominant terms of $G_\beta\{x^{1/\alpha} e^{2\pi\iota\mu/\alpha}\,;\alpha\theta\}$.

Hence when $0 < \alpha < 2$, and $|\arg x| < \alpha\pi/2$, we have asymptotically

$$E_\alpha(x\,;\theta,\beta) = \alpha^{\beta-1} \frac{\exp\{x^{1/\alpha}\}}{x^{\beta/\alpha}} \sum_{n=0}^{\infty} \frac{{}_\theta c_n \Gamma(1-\beta)}{x^{n/\alpha}\, \Gamma(1-\beta-n)},$$

where ${}_\theta c_n$ is given by the expansion

$$[\log(1-y)]^{\beta-1} (1-y)^{\alpha\theta-1} = (-y)^{\beta-1} \sum_{n=0}^{\infty} {}_\theta c_n (-y)^n,$$

valid when $|y| < 1$.

And when $\alpha \geqq 2$, we have asymptotically for all values of $|\arg x|$

$$\mathrm{E}_\alpha(x\,;\theta,\beta] = \alpha^{\beta-1}\sum_{\mu=-p}^{p}\left[\frac{\exp\{x^{1/\alpha}e^{\frac{2\pi\iota\mu}{\alpha}}\}}{x^{\beta/\alpha}e^{2\pi\iota\mu\beta/\alpha}}\sum_{n=0}^{\infty}\frac{{}_\theta c_n\Gamma(1-\beta)}{x^{n/\alpha}e^{2\pi\iota\mu n/\alpha}\Gamma(1-\beta-n)}\right],$$

wherein μ takes all integral values, positive, negative, or zero, such that

$$2\pi\mu+\arg x \leqq \tfrac{1}{2}\alpha\pi.$$

Part IX.

The Function ${}_1\mathrm{F}_1\{\alpha\,;\rho\,;x\}$.

§ 50. Generalised hypergeometric functions form a wide class of integral functions whose asymptotic expansions are closely connected with the theory of linear differential equations.

The general type of such series is

$$1+\frac{\alpha_1\ldots\alpha_p}{1\,.\,\rho_1\ldots\rho_q}x+\frac{\alpha_1(\alpha_1+1)\ldots\alpha_p(\alpha_p+1)}{1\,.\,2\,.\,\rho_1(\rho_1+1)\ldots\rho_q(\rho_q+1)}x^2+\ldots$$
$$=\frac{\Gamma(\rho_1)\ldots\Gamma(\rho_q)}{\Gamma(\alpha_1)\ldots\Gamma(\alpha_p)}\sum_{n=0}^{\infty}\frac{\Gamma(\alpha_1+n)\ldots\Gamma(\alpha_p+n)}{\Gamma(n+1)\Gamma(\rho_1+n)\ldots\Gamma(\rho_q+n)}x^n,$$

wherein $p \leqq q$.

This series we shall denote by ${}_p\mathrm{F}_q\{\alpha_1,\ \ldots,\ \alpha_p\,;\rho_1,\ \ldots,\ \rho_q\,;x\}$ or briefly by ${}_p\mathrm{F}_q\{x\}$.

The series satisfies the differential equation

$$\left\{(\vartheta+\alpha_1)\ldots(\vartheta+\alpha_p)-\frac{d}{dx}(\vartheta+\rho_1-1)\ldots(\vartheta+\rho_q-1)\right\}y=0 \quad . \quad . \quad . \quad (1),$$

where $\vartheta = x\dfrac{d}{dx}$. The equation is of order $(q+1)$, and the other q solutions are given by

$$x^{1-\rho_1}{}_p\mathrm{F}_q\{\alpha_1-\rho_1+1,\ \ldots,\ \alpha_p-\rho_1+1\,;2-\rho_1,\ \rho_2-\rho_1+1,\ \ldots,\ \rho_q-\rho_1+1\,;x\},$$

and $(q-1)$ similar functions.

I give here some of the results which I have obtained by applying integrals of the types previously used to the theory of these series. For detailed investigations I refer to a forthcoming paper.*

I. The series ${}_1\mathrm{F}_1\{\alpha\,;\rho\,;x\}$ satisfies the equation

$$x\frac{d^2y}{dx^2}-(x-\rho)\frac{dy}{dx}-\alpha y=0.$$

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* 'Cambridge Philosophical Transactions,' vol. 20.

An independent solution of this equation is

$$x^{1-\rho}{}_1F_1(\alpha-\rho+1\,;2-\rho\,;x).$$

II. By considering the contour integral $-\dfrac{1}{2\pi\iota}\displaystyle\int\Gamma(n-s)\,x^s\,ds$, we may show that

$${}_1F_1\{\alpha\,;\rho\,;x\} = e^x{}_1F_1\{\rho-\alpha\,;\rho\,;-x\}.$$

This result is valid for all values of arg x. It has been otherwise obtained by ORR.

III. By considering the contour integral

$$-\frac{1}{2\pi\iota}\int\frac{\Gamma(-s)\,\Gamma(\alpha+s)\,(-x)^s}{\Gamma(\rho+s)}\,ds,$$

we may show that, when $\mathfrak{R}(x)<0$, ${}_1F_1\{\alpha\,;\rho\,;x\}$ admits the asymptotic expansion

$$[\{\Gamma(\rho)/\Gamma(\rho-\alpha)\}](-x)^{-\alpha}{}_2F_0\left\{\alpha,\ 1-\rho+\alpha\,;-\frac{1}{x}\right\}.$$

IV. Combining II. and III., we show that, when $\mathfrak{R}(x)>0$, ${}_1F_1\{\alpha\,;\rho\,;x\}$ admits the asymptotic expansion

$$\frac{e^x\Gamma(\rho)}{\Gamma(\alpha)\,x^{\rho-\alpha}}\,{}_2F_0\left\{\rho-\alpha,\ 1-\alpha\,;\frac{1}{x}\right\}.$$

V. The combination of III. and IV. gives us the complete asymptotic expansion of ${}_1F_1\{\alpha\,;\rho\,;x\}$.

This I have verified by means of integrals taken round double loop contours of POCHHAMMER'S type.

VI. It is possible to take such a linear combination of the two solutions

$${}_1F_1\{\alpha\,;\rho\,;x\}\quad\text{and}\quad{}_1F_1\{\alpha-\rho+1\,;2-\rho\,;x\}\,x^{1-\rho}$$

as will admit all round $x=\infty$ the single asymptotic expansion

$$(-x)^{-\alpha}{}_2F_0\{\alpha,\ 1-\rho+\alpha\,;-1/x\}.$$

By considering the contour integral

$$\frac{1}{2\pi\iota}\int\Gamma(-s)\,\Gamma(1-\rho-s)\,\Gamma(\alpha+s)\,x^s\,ds$$

we can, in fact, prove that, when $|\arg x|<3\pi/2$,

$$\Gamma(\alpha)\,\Gamma(1-\rho)\,{}_1F_1\{\alpha\,;\rho\,;x\}+\Gamma(\alpha+1-\rho)\,\Gamma(\rho-1)\,x^{1-\rho}{}_1F_1\{\alpha-\rho+1\,;2-\rho\,;x\}$$
$$=x^{-\alpha}\Gamma(\alpha)\,\Gamma(1+\alpha-\rho)\,{}_2F_0\{\alpha,\ 1+\alpha-\rho\,;-1/x\}.$$

This theorem is equivalent to two different results when $\mathfrak{R}(x)<0$. By this means we can obtain III. anew.

VII. Similarly, when $|\arg x| < 3\pi/2$, we have

$$\frac{\Gamma(1-\rho)}{\Gamma(1-\alpha)}\,{}_1F_1\{\alpha\,;\rho\,;\,-x\} + \frac{\Gamma(\rho-1)}{\Gamma(\rho-\alpha)}\,x^{1-\rho}{}_1F_1\{1-\rho+\alpha\,;2-\rho\,;\,-x\}$$
$$= e^{-x}x^{\alpha-\rho}{}_2F_0\left\{\rho-\alpha,\ 1-\alpha\,;\,-\frac{1}{x}\right\}.$$

VIII. If we put $\alpha = 1$, we obtain the function $F_\rho(x) = \sum_{n=0}^{\infty} \frac{x^n\Gamma(\rho)}{\Gamma(\rho+n)}$. For this function we obtain, when $|\arg x| < \pi$, the asymptotic equality

$$F_\rho(x) = e^x x^{1-\rho}\Gamma(\rho) - \sum_{n=1}^{\infty} \frac{(\rho-1)\ldots(\rho-n)}{x^n}.$$

This result can be otherwise obtained from the equality

$$F_\rho(x) = 1 + xe^x \int_0^1 e^{-xy}y^{\rho-1}\,dy.$$

PART X.

The Function ${}_0F_1\{\rho\,;\,x\}$.

§ 51. I. The function ${}_0F_1\{\rho\,;\,x\} = \Gamma(\rho)\sum_{n=0}^{\infty}\frac{x^n}{\Gamma(n+1)\,\Gamma(\rho+n)}$, wherein ρ may have any value which is not zero or a negative integer, satisfies the differential equation

$$x\frac{d^2y}{dx^2} + \rho\frac{dy}{dx} - y = 0.$$

A second independent solution is $x^{1-\rho}{}_0F_1\{2-\rho\,;\,x\}$. Evidently the function is substantially BESSEL'S function.

We have

$$J_n(z) = \frac{1}{\Gamma(n+1)}(\tfrac{1}{2}z)^n\,{}_0F_1\{n+1\,;\,-\tfrac{1}{4}z^2\}.$$

II. By considering the contour integral $-\frac{1}{2\pi\iota}\int \Gamma(2n-s)\,(4x)\,\tfrac{1}{2}s\,ds$, we prove that

$${}_0F_1\{\rho\,;\,x\} = e^{-2x^{1/2}}{}_1F_1\{\rho-\tfrac{1}{2}\,;\ 2\rho-1\,;\ 4x^{1/2}\}$$
$$= e^{2x^{1/2}}{}_1F_1\{\rho-\tfrac{1}{2}\,;\ 2\rho-1\,;\ -4x^{1/2}\}.$$

This result is valid for all values of $\arg x$, and for the case of real variables was first established by KUMMER.

By means of this theorem we deduce the theory of the function ${}_0F_1\{\rho\,;\,x\}$ from the theory of the function ${}_1F_1\{\alpha\,;\,\rho\,;\,x\}$ developed in Part IX.

III. For all values of arg x we have the asymptotic expansion

$$
{}_0F_1\{\rho\,;\,x\} = e^{2x^{1/2}}\frac{\Gamma(2\rho-1)}{\Gamma(\rho-\frac{1}{2})}(4x^{1/2})^{1/2-\rho}{}_2F_0\left\{\rho-\tfrac{1}{2},\,\tfrac{3}{2}-\rho\,;\,\frac{1}{4x^{1/2}}\right\}
$$

$$
+\,e^{-2x^{1/2}}\frac{\Gamma(2\rho-1)}{\Gamma(\rho-\frac{1}{2})}(-4x^{1/2})^{1/2-\rho}{}_2F_0\left\{\rho-\tfrac{1}{2},\,\tfrac{3}{2}-\rho\,;\,\frac{1}{4x^{1/2}}\right\}.
$$

We take that value of $(4x^{1/2})^{1/2-\rho}$ which is equal to $\exp\{(\frac{1}{2}-\rho)\log(4x^{1/2})\}$, the logarithm being real when x is real and positive and having a cross-cut along the negative half of the real axis. Similarly $(-4x^{1/2})^{1/2-\rho}$ is equal to $\exp\{(\frac{1}{2}-\rho)\log(-4x^{1/2})\}$ when the logarithm is real, when x is real and negative and has a cross-cut along the positive half of the real axis.

IV. We may deduce the asymptotic behaviour of **Bessel's** function.

The theorem, though its expression is more concise, is equivalent to the results obtained by **Stokes**.

V. By considering the integral $-\frac{1}{2\pi\iota}\int\Gamma(-s)\,\Gamma(1-\rho-s)\,x^s\,ds$ we may prove that, if $|\arg x| < \pi$,

$$
\Gamma(1-\rho)\,{}_0F_1\{\rho\,;\,x\}+x^{1-\rho}\,\Gamma(\rho-1)\,{}_0F_1\{2-\rho\,;\,x\}
$$

$$
=\sqrt{\pi}x^{(1-2\rho)/4}e^{-2x^{1/2}}{}_2F_0\{\tfrac{3}{2}-\rho\,;\,\rho-\tfrac{1}{2}\,;\,-\tfrac{1}{4}x^{-1/2}\}.
$$

Part XI.

The Generalised Hypergeometric Functions.

§ 52. When $p \,\overline{<}\, q$, the generalised hypergeometric functions are integral functions. We limit ourselves to this case.

I. By considering the contour integral

$$
-\frac{1}{2\pi\iota}\int\frac{\Gamma(-s)\,\Gamma(\alpha_1+s)\,\Gamma(1-\rho_1-s)\ldots\Gamma(1-\rho_q-s)}{\Gamma(1-\alpha_2-s)\ldots\Gamma(1-\alpha_p-s)}x^s\,ds
$$

we may show that the linear combination of functions,

$$
\frac{\Gamma(\alpha_1)\,\Gamma(1-\rho_1)\ldots\Gamma(1-\rho_q)}{\Gamma(1-\alpha_2)\ldots\Gamma(1-\alpha_p)}\,{}_pF_q\{\alpha_1,\ldots,\,\alpha_p\,;\,\rho_1,\ldots,\,\rho_q\,;\,(-)^{p-q}x\}
$$

$$
+\,\frac{\Gamma(\alpha_1-\rho_1+1)\,\Gamma(\rho_1-1)\,\Gamma(\rho_1-\rho_2)\ldots\Gamma(\rho_1-\rho_q)}{\Gamma(\rho_1-\alpha_2)\,\Gamma(\rho_1-\alpha_3)\ldots\Gamma(\rho_1-\alpha_p)}x^{1-\rho_1}
$$

$$
{}_pF_q\{\alpha_1-\rho_1+1,\ldots,\,\alpha_p-\rho_1+1\,;\,2-\rho_1,\,1-\rho_1+\rho_2,\ldots,\,1-\rho_1+\rho_q\,;\,(-)^{p-q}x\}
$$

$+ (q-1)$ other terms similar to the last, admits the asymptotic expansion

$$\frac{\Gamma(\alpha_1)\,\Gamma(\alpha_1-\rho_1+1)\ldots\Gamma(\alpha_1-\rho_q+1)}{\Gamma(1-\alpha_2+\alpha_1)\ldots\Gamma(1-\alpha_p+\alpha_1)}\,x^{-\alpha_1}$$

$$\times\,{}_{q+1}\mathrm{F}_{p-1}\left\{\alpha_1,\ \alpha_1-\rho_1+1,\ldots,\ \alpha_1-\rho_q+1\,;\ \alpha_1-\alpha_2+1,\ldots,\ \alpha_1-\alpha_p+1\,;\ -\frac{1}{x}\right\},$$

provided $|\arg x| < \frac{1}{2}(q-p+3)\,\pi$.

There are evidently p relations similar to the one just written, each corresponding to an asymptotic solution of the differential equation (1) of p in the neighbourhood of $x=\infty$. There are therefore $q+1-p$ other asymptotic solutions near $x=\infty$ which will be asymptotic expansions of other linear combinations of the $q+1$ fundamental hypergeometric functions.

[II.] The linear combination of hypergeometric functions

$$\frac{\prod\limits_{r=1}^{q}\Gamma(1-\rho_r)}{\prod\limits_{r=1}^{p}\Gamma(1-\alpha_r)}\,{}_p\mathrm{F}_q\{\alpha_1,\ldots,\ \alpha_p\,;\ \rho_1,\ldots,\ \rho_q\,;\ (-)^{-p+1+q}x\}$$

$$+\sum_{r=1}^{q}x^{1-\rho_r}\,\frac{\Gamma(\rho_r-1)\prod\limits_{t=1}^{q}{}'\,\Gamma(\rho_r-\rho_t)}{\prod\limits_{t=1}^{p}\Gamma(\rho_r-\alpha_t)}\,{}_p\mathrm{F}_q\{1-\alpha_1-\rho_r,\ldots,\ 1+\alpha_p-\rho_r\,;$$

$$2-\rho_r,\ldots,\ \rho_q-\rho_r+1\,;\ (-)^{q+1-p}x\}$$

can be expressed by the contour integral

$$\mathrm{I} = -\frac{1}{2\pi\iota}\int\frac{\Gamma(-s)\prod\limits_{r=1}^{q}\Gamma(1-\rho_r-s)}{\prod\limits_{r=1}^{p}\Gamma(1-\alpha_r-s)}\,x^s\,ds,$$

and provided $|\arg x| < (q+1-p)\,\pi/2$, this integral may be taken along a line in the finite part of the plane parallel to the imaginary axis.

If $q+1-p=\mu$, we obtain

$$\exp\{\mu x^{1/\mu}\}\,(2\pi)^{(1-\mu)/2}\mu^{1/2}\,\mathrm{I} = -\frac{1}{2\pi\iota}\int \mathrm{S}(s)\,x^s\,ds,$$

where

$$\mathrm{S}(s) = \sum_{t=0}^{\infty}\frac{\Gamma(-s+t/\mu)\prod\limits_{r=1}^{q}\Gamma(1-\rho_r+t/\mu-s)}{\prod\limits_{r=1}^{\mu}\Gamma\left(\dfrac{t+r}{\mu}\right)\prod\limits_{r=1}^{p}\Gamma\left(1-\alpha_r+\dfrac{t}{\mu}-s\right)},$$

when

$$\mathfrak{R}(s) > \mathfrak{R}\left\{\frac{\mu-1}{2}+\alpha_1+\ldots+\alpha_p-\rho_1-\ldots-\rho_q\right\}/\mu.$$

We can infer that asymptotically, when $|x|$ is large,

$$\mathrm{I} = \exp\{-\mu x^{1/\mu}\}(2\pi)^{(\mu-1)/2}\mu^{-1/2}x^{\{\Sigma a-\Sigma\rho+(\mu-1)/2\}/\mu}\mathrm{J}(x),$$

where $|\mathrm{J}(x)|$ tends to unity as $|x|$ tends to infinity.

The complete asymptotic expansion is thus made to depend upon the determination of the singularities of $\mathrm{S}(s)$.

The relation obtained holds when $|x^{1/\mu}| < \pi$, and is thus equivalent to $q+1-p$ independent relations.

In this way the $(q+1)$ asymptotic expansions of the differential equation for the generalised hypergeometric equation are connected with the solutions which are integral functions in the finite part of the plane. The results agree with those of **Orr**; the methods, however, which have been suggested enable us to dispense entirely with his elaborate analysis.

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A DISCUSSION OF ATMOSPHERIC ELECTRIC POTENTIAL RESULTS AT KEW FROM SELECTED DAYS DURING THE SEVEN YEARS 1898 TO 1904

BY

C. CHREE, Sc.D., LL.D., F.R.S.

RAL HISTORY

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VI. *A Discussion of Atmospheric Electric Potential Results at Kew from Selected Days during the Seven Years* 1898 *to* 1904.

By C. Chree, *Sc.D., LL.D., F.R.S.*

(*From the National Physical Laboratory.*)

Received February 21,—Read March 15, 1906.

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§ 1. In 1894 special observations were commenced with the object of determining the influence of its position on the records from the Kew water-dropping electrograph, and also of ascertaining whether any alterations were desirable. The results were discussed in a paper[*] communicated to the Society in 1896.

The experiments led to certain changes in the apparatus, and an auxiliary system of eye observations was introduced with the object of obtaining quantitative results possessing a definite significance.

The original water tank was replaced by another of much larger diameter and small depth. The new tank is situated on the wooden roof of a detached portion of the north-west room on the ground floor, which contains the recording part of the electrograph. The wire connecting the water-dropping tube to the electrograph is much shorter than under the old arrangement, thus reducing the risk of defective insulation. Again, the down tube from the tank to the horizontal discharge tube is about $5\frac{1}{3}$ feet long, instead of a few inches as formerly, so that the pressure under which the jet issues is practically constant.

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[*] 'Roy. Soc. Proc.,' vol. 60, 1896, pp. 96–132.

Lastly, the jet is emitted parallel to the wall of the building, instead of perpendicular to it as before. This tends to increased uniformity in the conditions, as the potential varies rapidly in the direction perpendicular to the building, but little, if at all, in a horizontal direction taken parallel to it. The discharge tube, which projects from a window in the west wall, is situated about 10 feet to the north of the old tube, but nearly at the same level above the ground.

A flower border used to run the whole length of the west wall, containing shrubs 3 or 4 feet high. The northern half of this border was cleared of shrubs and laid down in grass, which has been kept short the whole year round. These changes were made with the object of securing that no appreciable fictitious element should be introduced into the annual change of potential gradient.

A definite test of the insulation of the apparatus was introduced, and is applied each morning. It is not always possible to improve defective insulation immediately when discovered, but at the worst the test shows when a day's record is to be regarded with suspicion.

The surface of the ground outside the building is not absolutely level, so the height of the spot where the jet breaks into drops can hardly be given with mathematical precision. It is very approximately 11 feet (3·35 metres). The perpendicular distance from the general outline of the west wall is $50\frac{1}{8}$ inches (127·3 centims.).

§ 2. If these distances, the environment, and the insulation of the apparatus could be kept absolutely uniform, the potential recorded on the electrograms would only require multiplication by an absolute constant to become converted into potential gradient per metre of height in the open. This ideal is not, however, practically attainable, and experience showed the desirability of obtaining a multiplier by reference to absolute eye observations made regularly in the open.

The eye observations are taken with a Kelvin portable electrometer, supported on a small level platform having three vertically projecting points, which prevent the electrometer from slipping. The platform is carried on a brass rod, fitting inside a hollow brass tube sunk in the ground. The rod can be raised in the tube and clamped at any convenient height. The original idea was to observe at two heights, a given distance apart. Having regard, however, to time and other considerations, it has been judged best not to vary the level, and the electrometer fuse has been used in a horizontal position at a fixed height above the ground. Thus the potential observed has referred to a fixed level, approximately 1·465 metres above the general level of the ground in the immediate vicinity. The ground is practically flat for a considerable space round the stand. The adjacent grass is kept short, and there is no tree, shrub, or building within what seems a reasonably satisfactory distance.

If P_1 be the potential shown by the portable electrometer, and P_2 that shown by the electrograph at the same instant, $P_1 \div (1{\cdot}465\ P_2)$ is a value for the factor by which the potential shown by the electrograph is to be multiplied to convert curve potentials into volts per metre of height in the open. Observations are taken with the portable electrometer nearly every day when the weather allows, and a mean value for the factor is calculated from each month's comparisons.

§ 3. When potential changes are very sudden, readings from the electrograph are doubtless partly dependent on its electrical capacity, and when the changes are very large, part of the trace is pretty sure to be lost. These large and sudden changes are mostly confined to times of rainfall, being specially prominent during thunderstorms. Further, during rain, drops are falling from all parts of the efflux tube, so that its record may not be solely, or possibly even mainly, determined by the jet at the end. For these and other reasons, it was decided to confine the tabulation of the electrograms to days when there was no rainfall, and to be content with 10 days a month. In selecting the 10 days one aimed at distributing them throughout the month, avoiding days in which negative potential was recorded, or there was reason to suspect the insulation. In some months there was a considerable excess of days to choose from, but in others it was difficult, and in a few cases impossible, to get as many as 10 suitable days. In one very wet month, in order to secure even 8 days, it was necessary, in two or three instances, to take in place of the natural day successive periods of 24 hours, comprising parts of two successive days. With this exception, a day always meant 24 hours, extending from midnight to midnight, G.M.T. All the data, except in Table IX., refer to Greenwich time, but the difference from this of local time is only $1\frac{1}{4}$ minutes.

Since 1902 the Annual Reports of the Observatory Department of the National Physical Laboratory have contained tables showing the mean monthly diurnal variation of the potential gradient from the selected days. Potential gradient is an exceptionally fluctuating element, and measurements of the actual photographic trace, taken at exact hours, may be far from representative of the mean value during 60 consecutive minutes. The practice adopted has been to draw in pencil a continuous curve, following as nearly as the eye can judge the general trend of the trace, and to measure the ordinates of this curve at exact hours, G.M.T.

During the past two years, the data for earlier years have been similarly treated, and the present paper deals with the results from the seven years 1898 to 1904.

Mean Monthly and Annual Values of the Potential Gradient.

§ 4. Table I. gives the mean value of P (the potential gradient in the open in volts per metre) for each individual month and for each year, and likewise the mean annual inequality based on the seven years' results. The annual inequality is exhibited graphically in fig. 1 by the continuous line curve; the ordinates represent the mean values of P for the individual months, expressed as fractions of their arithmetic mean from the 12 months.

TABLE I.—Potential Gradient (Volts per Metre).

	1898.	1899.	1900.	1901.	1902.	1903.	1904.	Mean.
January . . .	174	285	189	238	164	162	194	201
February . .	244	298	182	247	232	174	190	224
March . . .	216	203	180	141	152	191	177	180
April	109	139	107	140	149	165	160	138
May	97	151	96	127	93	167	130	123
June	104	105	73	114	115	156	106	111
July	104	90	86	95	86	105	117	98
August . . .	125	127	104	87	111	129	118	114
September . .	163	83	118	117	104	135	130	121
October . . .	161	175	133	191	123	141	147	153
November . .	250	167	157	215	178	172	259	200
December . .	184	328	263	162	237	250	273	243
Mean . .	161	179	141	156	145	162	167	159

Table I. shows at once how variable an element P is. It is at least doubtful whether even seven years are sufficient to give an annual inequality which can be relied on as fully representative in its details. There is unquestionably a well-marked minimum near midsummer. There seems also to be a second minimum in January, but whether this would be shown—or if shown would be as prominent—if we had 70 years instead of 7 is open to doubt. The fact that the largest mean monthly value did not occur in January in any one of the seven years, whilst occurring four times in December, is so far confirmatory. In November, December, and January, however, fog is a very uncertain while very important influence. During thick fog in winter P is usually abnormally high, 400 to 600 volts—or practically double the ordinary gradient—being not infrequently met with. Thus in winter the mean value of P varies much from day to day even in fair weather. For instance, in December, 1898, the last three of the selected days gave a mean value for P of 380 volts, whilst the corresponding mean from the first seven days only slightly exceeded 100 volts. So, again, in January, 1899, the mean values of P from the first five and the last five of the selected days were roughly 160 and 400 volts respectively. The figures in Table I. itself, *e.g.*, those for December in the years 1899 and 1901, afford examples almost as striking.

The mean value for the year appears lower for the three consecutive years 1900 to 1902—which cover the period of sun-spot minimum—than for the others. As this phenomenon also appears when we confine ourselves to the six summer months, April to September, when climatic influences are comparatively uniform, it *may* be a real one. If so, P tends to be *lower* than usual near sun-spot minimum. The difference shown, however, in Table I. may be accidental; it is certainly too small to rely on, considering the limited number of years and the many sources of uncertainty.

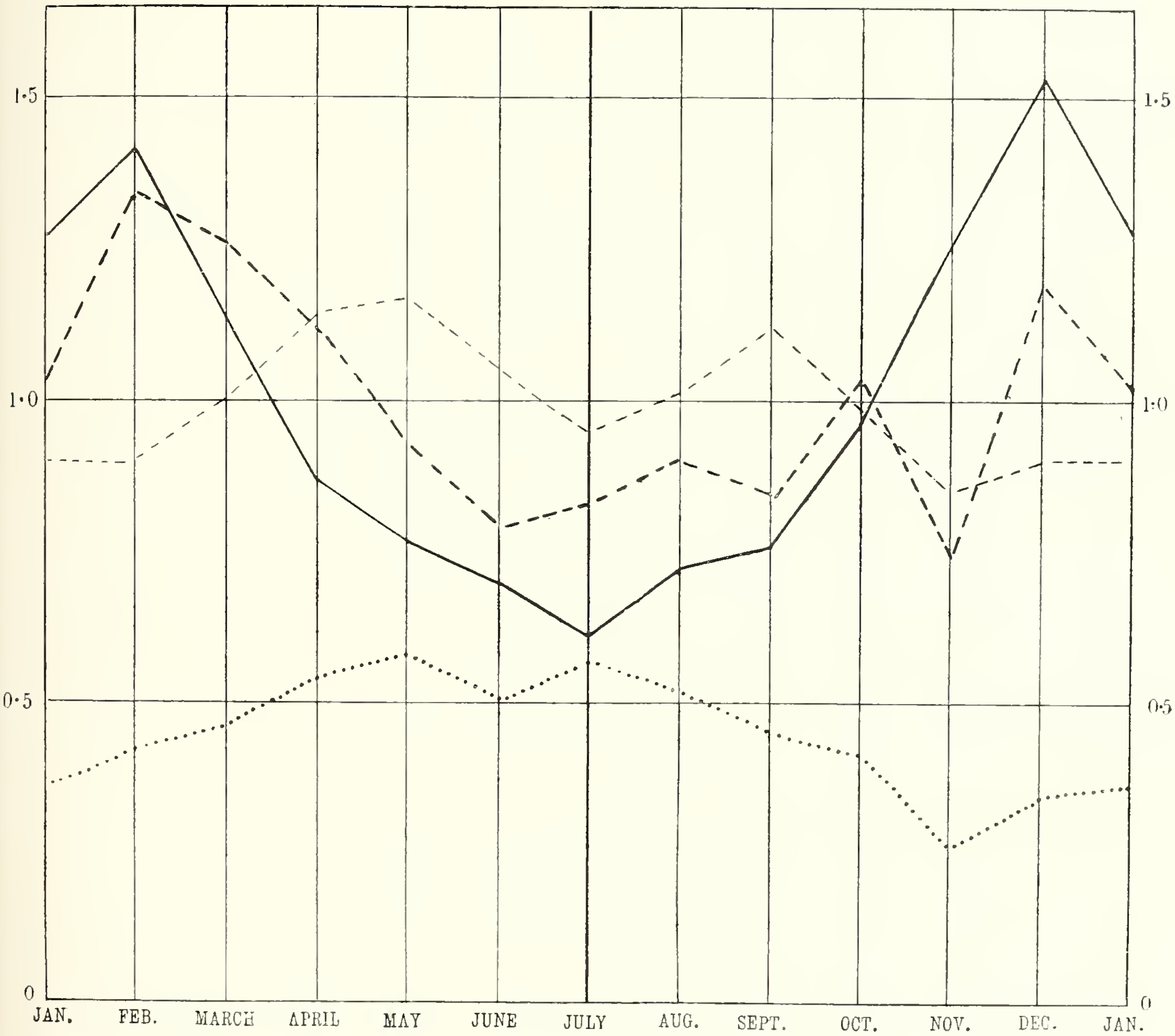

Fig. 1.

——— Mean monthly values of potential gradient.
········· (Daily range) ÷ (mean monthly value).
— — — Sum 24 hourly differences potential gradient.
- - - - - Sum 24 hourly differences barometric pressure.

Non-cyclic Effect.

§ 5. In meteorological elements such as temperature, where there is a conspicuous annual variation, there is, at certain seasons of the year, a steady tendency to an increase, and at other seasons to a decrease, during the 24 hours.

In such a case the value assigned to midnight in the mean data for a particular month varies slightly according as one makes midnight the first or the last hour of the day.

When, instead of all the days in the month, one takes a limited number of a particular kind, a non-cyclic, or a-periodic, element may present itself in the diurnal inequality, though there is no such element present to an appreciable extent in the average day of the month. This phenomenon, for instance, as I have pointed out, is conspicuous in the horizontal component of the earth's magnetic field on magnetically "quiet" days.

There are two courses open in such a case, viz., to give the mean hourly values taken direct from the observations, with data for *both* midnights, or else to eliminate the non-cyclic element from the diurnal variation while stating its amount.

The latter course has been adopted here. The size of the *algebraic* mean non-cyclic element for the selected days in individual months is recorded in Table II., in volts per metre.

Table II. shows on the whole a rise of P throughout the average selected day, but the mean value of the non-cyclic element is very small, and its sign even varies from year to year. Coming to individual months, we see that in May the non-cyclic effect was negative in six out of the seven years; but in three years, 1900, 1901, and 1903, there were more individual days in which it was plus than minus. The only months in which there seems a decided tendency for P to rise during the 24 hours of a selected day are December and January. In the former month 42 days out of 68, and in the latter month 38 days out of 65, showed a rise. In December there was an excess of days showing a plus effect in six years out of the seven.

TABLE II.—Non-cyclic Effect (Volts per Metre).

	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	December.	Year.
1898	+17	−17	+ 8	− 6	−25	+ 4	+23	+ 9	+ 4	+39	−22	+ 1	+ 3
1899	+11	− 4	−51	+ 8	−12	+14	+12	−14	− 8	+18	+ 8	+30	+ 1
1900	−39	+ 8	+40	+ 8	− 2	+12	− 2	+ 3	− 4	+ 9	+11	+29	+ 6
1901	+ 9	+17	−33	+21	−22	− 5	−13	− 2	− 8	−11	+20	+50	+ 2
1902	+26	+ 3	+54	+15	− 4	+22	− 1	−16	−11	+26	+11	+ 4	+11
1903	+64	−23	− 2	−11	+ 7	+ 6	− 6	−21	−12	−32	−10	+12	− 3
1904	+25	−17	0	− 9	−18	− 6	−18	− 9	−14	−18	−24	+34	− 6
Mean	+16	− 5	+ 2	+ 4	−11	+ 7	− 1	− 7	− 8	+ 4	− 1	+23	+ 2

Diurnal Inequality.

§ 6. Table III. shows the mean diurnal inequality—after elimination of the non-cyclic effect—for the individual months and the year, and also for three seasons, viz., Winter (November to February), Equinox (March, April, September and October) and Summer (May to August). Each hourly value depends on approximately 70 readings, and as these were taken to at least the nearest 10, sometimes the nearest 5 volts, the table gives the results to the nearest 0·1 volt. Distinct maxima and minima appear in heavy type.

The *ranges* in the penultimate column represent the excess of the largest mean hourly value over the smallest. The last column gives the sum of the 24 hourly differences from the mean for the day to the nearest volt.

The diurnal inequalities for the individual months and the year are illustrated by the curves in fig. 2 which are all drawn to a common scale. They pass through all the observational points and thus enable the reader to judge for himself of the sufficiency of the data. The curve for the year and those for a majority of the months, notably April, June, August and October, possess a smoothness which leaves little to be desired. A few isolated observational points catch the eye, *e.g.*, 1 p.m. in January and in September. I have satisfied myself that the cause is not arithmetical error, but if the number of year's data were largely increased the outstanding values for individual hours would very probably disappear. In the four months November to February there is a slight flattening or depression of the curve shortly after the evening maximum which looks hardly natural. Whether this would disappear if a larger number of year's data were employed is, however, more doubtful. It seems to arise from a slight variability in the hour of maximum in the same month of different years.

The double daily period, though most prominent in summer, is shown clearly in every instance. December is the month showing the nearest approach to a single maximum and minimum, November and January coming next; but even in these three months there is not the slightest doubt as to the existence of an afternoon minimum, while the forenoon maximum exceeds that of the late afternoon in January and February, and is practically equal to it in December. The early morning minimum is the principal one only in the four midwinter months and in August and September. The equinoctial months show the afternoon minimum just about as prominently as the midsummer months.

The morning minimum occurs near 4 a.m., its time varying very little throughout the year. The afternoon minimum is only a little more variable, its time of occurrence falling usually near 2 p.m. The hours of maxima are rather more variable, the day interval between the two being less in the winter than in the summer months.

When, as in the present case, there is a well-marked double maximum and minimum, the amplitude of the range is probably not so satisfactory a measure of the activity of

Table III.—Diurnal Inequalities (Volts per Metre).

	Forenoon.												Afternoon.													
Hour . .	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	Range.	Sum of 24 differences.
January .	−20·4	−27·9	−34·7	−41·6	**−42·3**	−33·9	−13·7	+ 4·7	+21·0	**+30·6**	+17·7	+ 8·6	+ 5·3	− 3·7	**− 5·1**	+ 2·6	+15·6	+22·6	**+28·7**	+23·9	+21·3	+20·0	+ 9·3	− 8·9	72·9	464
February .	−19·5	−34·9	−45·7	**−51·7**	−48·9	−33·5	−15·1	+13·2	+34·6	**+42·3**	+27·8	+13·5	−10·8	**−18·8**	−13·1	− 5·5	+ 9·5	+22·9	**+35·3**	+35·1	+33·3	+25·9	+11·1	− 2·9	94·0	610
March. . .	− 2·0	−14·9	−26·8	**−31·5**	−26·5	−12·9	+ 5·2	+20·5	**+28·4**	+17·2	− 9·3	−25·3	−33·8	**−35·2**	−33·8	−24·6	−10·6	+12·0	+35·8	**+48·0**	+45·1	+41·0	+25·2	+ 8·5	83·2	574
April . . .	− 3·8	−11·5	−16·9	**−18·1**	−11·5	+ 4·8	+27·2	**+39·2**	+30·8	+12·1	−12·8	−26·6	−34·8	**−34·9**	−34·1	−27·8	−20·4	− 2·1	+19·8	+31·8	**+34·6**	+32·4	+18·8	+ 4·4	74·1	511
May. . . .	+ 6·4	− 0·9	− 8·8	**−11·9**	− 6·6	+ 2·7	+13·0	**+20·0**	+14·4	+ 2·2	−16·9	−25·8	−32·2	**−34·9**	−30·0	−24·0	−17·0	− 2·0	+16·8	+28·8	**+35·8**	+31·5	+24·5	+15·8	70·7	423
June . . .	− 3·5	−10·9	**−15·0**	−14·5	− 6·9	+ 1·8	+13·1	**+18·8**	+18·4	+12·8	− 0·2	−12·2	−21·9	−27·0	**−28·0**	−22·3	−15·5	− 2·2	+10·3	+22·7	**+28·7**	+28·1	+17·8	+ 7·3	56·7	360
July. . . .	− 9·2	−13·2	−14·5	**−17·3**	−10·2	+ 3·3	+21·4	**+29·3**	+27·4	+15·7	− 1·9	−11·6	−18·5	−23·6	**−25·0**	−20·9	−15·6	− 7·5	+ 4·3	+19·7	**+30·3**	+24·3	+12·4	+ 0·5	55·3	378
August . .	−10·1	−18·8	−26·5	**−27·1**	−19·6	− 5·2	+ 9·6	+21·1	**+24·8**	+14·4	+ 3·5	− 7·4	−15·6	−20·4	**−23·5**	−19·5	−10·4	+ 3·8	+18·4	+29·4	**+32·5**	+29·1	+17·8	− 0·4	59·6	409
September	−14·2	−17·4	−19·1	**−21·2**	−18·8	− 6·4	+ 7·0	+17·5	**+19·2**	+ 8·6	− 7·4	−14·2	−17·0	**−20·8**	−17·5	−12·2	− 0·7	+20·2	**+32·8**	+30·6	+27·2	+20·3	+ 7·9	− 3·1	54·0	381
October . .	−23·9	**−25·3**	−24·6	−23·4	−18·0	− 4·1	+14·4	+31·6	**+33·0**	+19·1	− 0·3	−14·3	−26·0	**−29·6**	−22·4	− 8·3	+ 7·7	+25·1	+31·7	**+32·7**	+26·9	+14·9	− 0·3	−17·6	62·6	475
November	−16·7	−23·8	**−26·9**	−24·5	−18·4	− 8·7	+ 1·3	+11·1	+13·2	**+15·8**	− 0·5	− 8·9	**−12·8**	− 9·5	− 1·5	+ 9·3	+22·6	**+24·8**	+23·6	+21·6	+19·5	+ 5·6	− 3·5	−13·7	51·7	338
December	−24·0	−37·4	−45·4	**−50·4**	−47·6	−36·1	−18·3	+ 6·3	+23·3	**+30·3**	+14·2	+ 7·6	+ 6·0	**+ 3·4**	+ 7·2	+16·2	+22·7	+23·7	**+31·7**	+27·0	+23·0	+17·9	+ 5·7	−13·0	82·1	543
Year . . .	−11·8	−19·8	−25·4	**−27·8**	−23·0	−11·1	+ 5·4	+19·4	**+24·0**	+18·4	+ 1·1	− 9·7	−17·7	**−21·3**	−18·9	−11·4	− 1·0	+12·2	+21·1	+29·3	**+29·8**	+24·2	+12·2	− 1·9	57·6	401
Winter . .	−20·1	−31·0	−38·2	**−42·0**	−39·3	−29·3	−11·4	+ 8·8	+23·0	**+29·8**	+14·8	+ 5·2	− 3·1	**− 7·1**	− 3·1	+ 5·7	+17·6	+24·8	**+29·8**	+26·9	+24·3	+17·4	+ 5·7	− 9·6	71·8	468
Equinox .	−11·0	−17·3	−21·9	**−23·5**	−18·7	− 4·7	+13·4	+27·2	**+27·9**	+14·2	− 7·5	−20·1	−27·9	**−30·1**	−26·9	−18·2	− 6·0	+13·8	+30·0	**+35·8**	+33·5	+27·1	+12·9	− 2·0	65·9	472
Summer .	− 4·1	−11·0	−16·2	**−17·7**	−10·8	+ 0·7	+14·3	**+22·3**	+21·2	+11·3	− 3·9	−14·3	−22·0	−26·5	**−26·6**	−21·7	−14·6	− 2·0	+12·5	+25·1	**+31·8**	+28·3	+18·1	+ 5·8	58·4	383

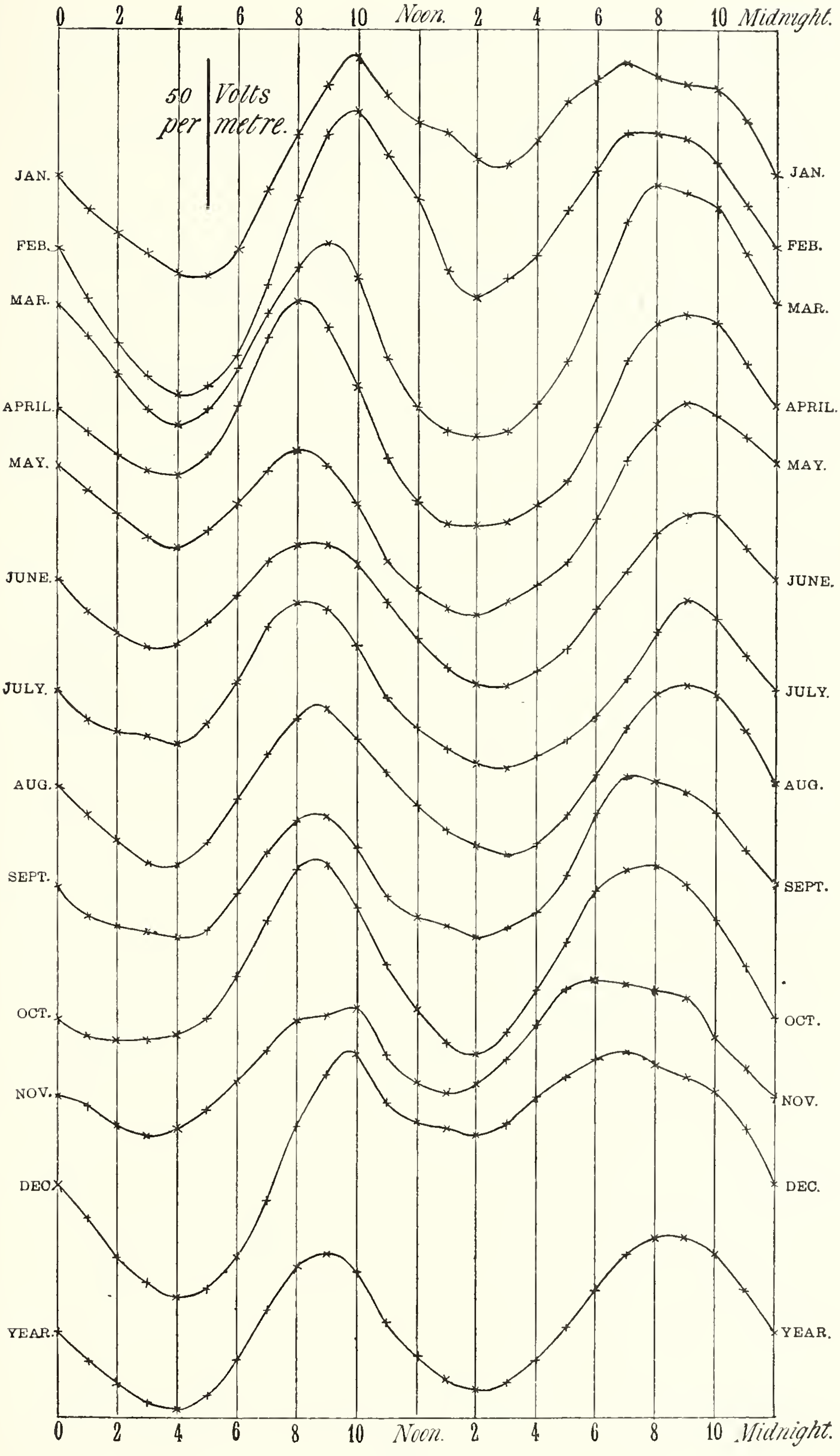
0
2
4
6
8
10
Noon.
2
4
6
8
10
Midnight.
50 per
Volts metre.
JAN.
FEB.
MAR.
APRIL.
MAY.
JUNE.
JULY.
AUG.
SEPT.
OCT.
NOV.
DEC.
YEAR.

Fig. 2.

the forces to which the diurnal inequality is due as is the size of the 24 hourly differences from the mean. Both these quantities, as recorded in Table III., agree in representing a maximum of activity in February and a minimum in November, though the latter month differs but little from June, July, August and September. The annual variation of the sum of the 24 differences is represented by the heavy broken line in fig. 1, unity representing the mean of the 12 monthly values.

§ 7. In view of theories as to the cause of the diurnal variation, interest attaches to the comparative size of the potential changes during the day and the night. The forenoon maximum and afternoon minimum occur at Kew when the sun is above the horizon, the afternoon maximum and the morning minimum when the sun is below the horizon. I have thus taken the difference between the first-mentioned maximum and minimum as a measure of the change of potential during the day, and the difference between the other maximum and minimum as a measure of the change of potential during the night, terming the first the "Day fall," the latter the "Night fall."

TABLE IV.

	Absolute values, volts per metre—		Ratios borne to corresponding mean monthly values of potential gradient by—		
	Day fall.	Night fall.	Day fall.	Night fall.	Range.
January	35·7	71·0	0·178	0·353	0·363
February	61·1	87·0	0·273	0·389	0·420
March	63·6	79·5	0·354	0·442	0·462
April	74·1	52·7	0·535	0·381	0·535
May	54·9	47·7	0·447	0·388	0·575
June	46·8	43·7	0·423	0·395	0·513
July	54·3	47·6	0·556	0·488	0·567
August	48·3	59·6	0·422	0·520	0·520
September	40·0	54·0	0·330	0·446	0·446
October	62·6	58·0	0·409	0·379	0·409
November	28·6	51·7	0·143	0·259	0·259
December	33·7	82·1	0·139	0·338	0·338
Arithmetic means for—					
Year	50·3	61·2	0·351	0·398	0·451
Winter	39·8	73·0	0·183	0·335	0·345
Equinox	60·1	61·0	0·407	0·412	0·463
Summer	51·1	49·7	0·462	0·448	0·544

Table IV. shows the day and night falls from the diurnal inequalities of the several months, and also the ratio borne by these two quantities and by the daily range to the mean monthly value of P. Considered absolutely, the day fall has a conspicuous minimum in the three months November to January, the night fall a conspicuous maximum from December to March. The regular causes, whatever they are, to which the day and night falls are due, are at Kew nearly equal in intensity in the average month both of equinox and summer.

The daily range when considered absolutely is, as we have already seen, greater in winter than summer; but relative to the mean value of P for the day, the day and night falls and the range all show a decided minimum in November, December and January. If the potential gradient is due to a negative charge on the earth, the density of that charge is on the average greater in winter than in summer, but the diminished charge of summer is, relatively considered, more influenced by the causes to which the regular diurnal inequality is due.

The figures in the last column of Table IV. are shown graphically in the dotted curve of fig. 1.

Analysis of Diurnal Inequality in Fourier Series.

§ 8. The diurnal inequalities in Table III. have been analysed in Fourier series

$$c_1 \sin (t+\alpha_1)+c_2 \sin (2t+\alpha_2)+c_3 \sin (3t+\alpha_3)+c_4 \sin (4t+\alpha_4),$$

where t represents time counted from midnight (G.M.T.), one hour being taken as equivalent to 15°. The amplitudes c_1, &c., and the phase angles α_1, &c., for the individual months, the year, and the three seasons are shown in Table V. In the case of the amplitudes, unity represents, as before, a potential gradient of one volt per metre. The variation of c_1 and c_2 throughout the year is illustrated by the heavier full and dotted line curves respectively of fig. 3. The ordinates represent the ratios borne by the monthly values to their arithmetic mean.

The annual variation of c_1 is of a most unusual character. The mid-winter maximum and mid-summer minimum are extraordinarily pronounced. The phase angle α_1 also shows a remarkable annual variation, the times of maximum in "summer" and "winter" differing by nearly 8 hours. In July and December the 24-hour waves are nearly in opposite phases.

The 12-hour term presents very different features. Its amplitude, c_2, is slightly less for winter than for summer, and there are maxima at the equinoxes, but the annual variation is comparatively small. The variation shown by the phase angle α_2 is also comparatively small, the difference between the times of maximum in winter and equinox being little over half an hour.

The 8-hour and 6-hour terms are so small that considerable uncertainty must attach to the results for individual months. Still, there is a regularity about the figures, especially those for the 8-hour term, which seems to justify our acceptance of at least the general features. The annual variation of c_3 is somewhat similar to

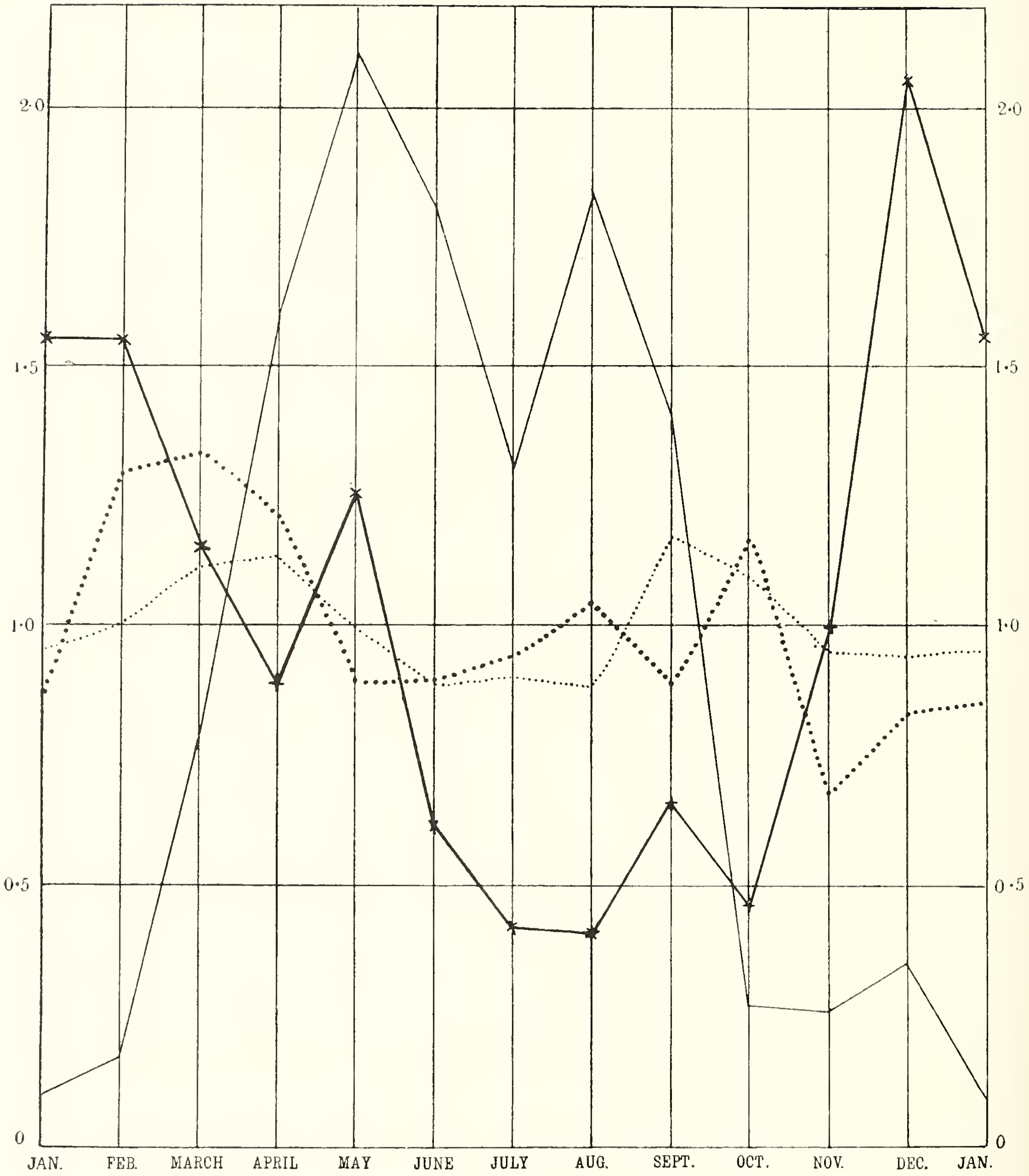

Fig. 3.

1 = mean of the twelve monthly values.

———	Annual variation of c_1 potential gradient.
———	„ „ c_1 barometric pressure.
●●●●●●●●●	„ „ c_2 potential gradient.
....	„ „ c_2 barometric pressure.

that of c_1, the values for the winter months being conspicuously greater than those for the summer months. There is also a fairly systematic annual variation in the phase angle α_3; but this angle is largest at the season when α_1 is least, and conversely. The 6-hour term shows an annual variation similar on the whole to that exhibited by the 12-hour term. In equinox and summer the 6-hour wave seems fully larger than the 8-hour wave.

TABLE V.—Diurnal Inequality. Amplitudes and Phase Angles.

	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
		° ′		° ′		° ′		° ′
January . .	22·33	206 5	21·50	169 42	6·82	10 36	1·87	234 39
February. .	22·32	203 37	32·72	170 55	10·31	9 6	2·64	224 36
March. . .	16·61	123 8	33·54	185 31	4·68	35 53	5·11	307 8
April . . .	12·79	71 39	30·57	192 33	4·78	96 17	6·28	313 55
May . . .	18·21	85 57	22·40	188 25	3·14	100 22	3·69	313 31
June . . .	8·98	78 52	22·57	182 45	1·32	124 59	1·40	276 49
July . . .	6·12	48 13	23·77	185 8	3·40	124 29	4·44	292 39
August . .	5·96	142 14	26·30	181 30	1·50	106 39	2·70	312 45
September .	9·50	153 51	22·63	198 45	2·93	16 15	3·51	329 46
October . .	6·58	191 52	29·60	205 46	6·35	18 21	3·25	288 23
November .	14·14	201 40	16·98	211 53	5·43	38 17	1·56	237 34
December .	29·69	208 24	21·09	175 12	7·11	35 44	2·89	249 3
Year . . .	8·40	165 4	24·75	186 50	3·82	39 29	2·80	292 38
Winter . .	22·10	205 32	22·23	178 50	7·21	21 8	2·21	236 50
Equinox . .	8·78	124 43	28·83	195 5	3·98	40 26	4·42	310 32
Summer . .	8·82	86 7	23·74	184 20	2·29	113 36	2·98	301 38

Annual Variation. Fourier Series.

§ 9. The annual variation may be represented by a series of the type

$$M + P_1 \sin(t+\theta_1) + P_2 \sin(2t+\theta_2) + \ldots,$$

where M is the arithmetic mean of the 12 monthly values, t is the time counted from the beginning of the year, 1 month being taken as equivalent to 30°, while $P_1, P_2, \ldots, \theta_1, \theta_2, \ldots$ are constants.

Table VI. gives for a variety of elements the values of the amplitudes and phase angles of the yearly and half-yearly terms, and the ratios borne by these amplitudes to the mean value of the element and to one another. As before, in the amplitudes unity represents 1 volt per metre. The angles are given only to the nearest degree.

The representation of the annual variation by two terms of the series is, as a matter of fact, not very close in any one of the elements. This may mean that other shorter period terms are by no means negligible, or merely that a larger number of year's data are necessary for high precision.

The annual term is, in all cases, the more important of the two. The relative importance of the semi-annual term is much greater for the day fall than for the other elements; it is least for the mean value for the day.

TABLE VI.—Annual Variation. Amplitudes and Phase Angles.

	P_1.	θ_1.	P_2.	θ_2.	P_1/M.	P_2/M.	P_2/P_1.
		°		°			
Mean value for the day	63·8	81	7·49	84	0·40	0·05	0·12
Sum 24 hourly differences . . .	92·0	44	26·7	315	0·20	0·06	0·29
Range	15·7	37	2·80	358	0·23	0·04	0·18
Day fall	11·3	342	8·95	267	0·22	0·18	0·79
Night fall	15·9	70	6·49	15	0·26	0·11	0·41
c_1 (diurnal inequality)	8·60	59	2·61	91	0·60	0·18	0·30
c_2 (,, ,,)	8·44	53	3·26	294	0·33	0·13	0·39

Comparison with Previous Results for Kew.

§ 10. In the 'Phil. Trans.' for 1868, pp. 347–361, atmospheric electricity data from Kew for a 2-year period (June, 1862, to May, 1864) were discussed by Professor J. D. EVERETT. The data were from all days of the year. EVERETT calculated Fourier coefficients corresponding to our c_1, c_2, α_1, α_2 for the mean diurnal inequality of each individual month, and for each of the two years, and then for the 12 months and the year from the two year's data combined. His amplitudes were expressed in terms of an arbitrary unit. The results for corresponding months of the two years vary somewhat largely, and there is considerable difference between the mean results for the two years. Thus even the values from the two year's data combined, at least those for individual months of the year, are clearly exposed to rather large uncertainties.

It should be noticed that EVERETT's hour angles (*loc. cit.*, p. 358) are counted from noon. Thus, in comparing his results with mine, 180° must be added to his E_1 (my α_1); his E_2 and my α_2 are immediately comparable. The following remarks apply to his values for the two years combined:—

My value for α_1 is above EVERETT's from September to February, the mean excess being 18° 1′, and below his from March to August, the mean deficiency being 27° 10′. In the mean diurnal inequality for the year, however, EVERETT's value for α_1 exceeds mine by only 1° 6′, corresponding to 4·4 minutes of time. As regards α_2, my value is above EVERETT's in six months, viz., May and July to November, the mean excess being 11° 7′, and below his in the other six months, the mean deficiency being 12° 40′. In the mean diurnal inequality for the year his value of α_2 exceeds mine by 2° 10′, answering to 4·3 minutes of time. The differences in the phase angles in the two investigations, though comparatively small, especially in the case of the 12-hour term, are too systematic to be ascribed to chance, but several explanations are possible.

EVERETT'S table on his p. 358 agrees with my Table V. in making c_1 (his A_1) greatest in December and January, and least in July and August; and his difference between the maximum and minimum values is even greater than mine. Also his largest values for c_2 (his A_2) occur, like mine, in February and March, his least values occurring in May, June, and November. There is thus a fairly close *general* resemblance between our results for the amplitudes. There is, however, a very important difference as regards the relative importance of c_1 and c_2. We have, in short,

	EVERETT (1862–4).	CHREE (1898–1904).
$\dfrac{\text{arithmetic mean of 12 monthly values of } c_2}{\text{arithmetic mean of 12 monthly values of } c_1} =$	0·85	1·75
$\dfrac{c_2 \text{ in mean diurnal inequality for the year}}{c_1 \text{ in mean diurnal inequality for the year}} =$	0·97	2·95

Some further aspects of this difference are considered later in § 13.

EVERETT also expressed the annual variation in the mean daily potential gradient as a Fourier series with annual and semi-annual terms. His times were measured from the middle of January, so that his phase angles (E_1 and E_2 in his notation) have to be diminished accordingly for comparison with mine. His results from the two years combined are in the notation of Table VI., counting time from the beginning of the year,

θ_1.	θ_2.	P_1/M.	P_2/M.	P_2/P_1.
90°	249°	0·36	0·02	0·05

EVERETT'S results for the annual term are thus fairly similar to mine, but he makes the amplitude of the semi-annual term even less than I do, and his value for its phase angle is quite different from mine. This is not, however, very surprising, as the phase angles for his two years taken separately differ by 100°, and the amplitude for the second year is only $\frac{3}{8}$ of that for the first. Also inspection of EVERETT'S annual variation curve in his plate XXI. shows that its representation by only annual and semi-annual terms must be very rough.

Comparison with CHAUVEAU'S *Results for other Stations.*

§ 11. The intercomparison of results from different stations is difficult owing to uncertainty as to the real significance of the units employed. The length and the height above ground of the discharge tubes of water droppers vary greatly. Some are in low, others in lofty buildings, so that even if all were of one length and at one height they would not give comparable results.

To meet this difficulty so far as possible, in the article on "Atmospheric Electricity" in the 10th edition of the 'Encyclopædia Britannica,' I expressed each hourly value in a diurnal inequality as a percentage of the mean value for the day.

The principal maximum and minimum, for example, in EVERETT'S mean diurnal inequality for the year at Kew were given as 139 and 71, and thence the range would be 68. In an important and very comprehensive paper,* Mr. A. B. CHAUVEAU has employed a method of representing the ranges which differs from the above only in taking the mean of the 24 hourly values as 1 instead of 100. He compares in particular what he calls day and night ranges (*amplitude diurne*, *amplitude nocturne*). For both ranges he takes the late evening maximum, so that

amplitude diurne = night maximum less afternoon minimum,

amplitude nocturne = night maximum less early morning minimum.

He did so because in all the cases he considered, with the single exception of Lyons, the evening maximum exceeded the forenoon maximum throughout the year.

Finding that at most places the diurnal inequality was nearly the same for May, June, July and August, CHAUVEAU obtains "summer" values for his day and night ranges from a diurnal inequality based on days selected from these four months. For corresponding winter values he usually confines himself to days selected from December and January only. In dealing, however, with the Bureau Central Météorologique in Paris—the station which he considers most fully—his winter includes as well days from late November and early February. CHAUVEAU also records the ratio borne by the mean value of P from the selected winter days to the corresponding summer value. In most cases he confines himself to fine weather days.

Table VII. summarises the chief results given by CHAUVEAU, with the addition of corresponding results for Kew from Tables I and III.

CHAUVEAU apparently regards the conditions at the Bureau Central as having somewhat deteriorated since 1893 through the growth of trees. As against this, the data there for 1893–4 depend on a somewhat limited number of days, and any single year may not be fully representative. The site at Perpignan is considered by CHAUVEAU amongst the best. As to Kew and Greenwich, I shall quote CHAUVEAU'S own words (*loc. cit.* p. C 52). "La modification progressive de la variation d'été dans les observations de M. EVERETT, de M. WHIPPLE et dans celles de Greenwich nous paraît être en rapport avec des conditions de moins en moins bonnes dans l'installation du collecteur."

The results at Greenwich and at the Collège de France show a rather striking similarity which CHAUVEAU notes, but he regards them both as abnormal in several respects.

A mean from the two sets of results for the Bureau Central presents fairly similar features to the latest Kew results, though both the day and night ranges appear to be larger at the former station. The Kew summer data are from the diurnal inequality in Table III. for the four summer months combined. If the quantities had been found for each of the months independently, the arithmetic means would have slightly exceeded the values in the table, viz., amplitude diurne 0·54, amplitude nocturne 0·45. The Kew results for winter are arithmetic means from December, January and February treated independently. Omitting February, the values would be less, viz., amplitude diurne 0·14, amplitude nocturne 0·35.

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* 'Annales du Bureau Central Météorologique de France,' Année, 1900, I Mémoires, pp. C 1 to C 120.

As regards the different Kew data, it should be taken into account that Birt's were obtained with the old Ronalds apparatus, the point at which the potential was measured being some 16 feet above the dome and more than 80 feet above the general level of the ground. Also the observations were from the even hours only, which inevitably leads to smaller ranges than when hourly observations are taken. Birt grouped his data in several classes. That taken by Chauveau included only low positive potentials, *i.e.*, excluded all cases where the potential was negative or exceptionally high. Everett's data included all readings positive or negative, Whipple's all but days of negative potential.

Table VII.—Abstract of Chauveau's Results and Comparison.

Place.	Period.	Mean length of tube. Metres.	Amplitude diurne.		Amplitude nocturne.		Ratio of mean values of potential gradient. Winter/Summer.
			Winter.	Summer.	Winter.	Summer.	
Lisbon	1884–7	0·85	0·28	0·41	0·87	0·69	2·15
Perpignan	1885–95	1·5	0·39	0·38	0·67	0·46	1·45
Florence	1885	1·75	0·48	0·46	0·78	0·61	1·38
Moncalieri	—	—	0·36	0·47	0·47	0·40	1·69
Lyons	1885–90	—	0·16	—	0·36	—	2·14
Parc St. Maur . . .	1889–90	—	0·34	0·65	0·58	0·52	1·29
Collège de France . .	1885–7	—	0·23	0·86	0·42	0·30	2·00
Eiffel Tower	1893	1·7	—	—	—	0·48	—
,, ,, ...	1896–8	0·55	—	—	—	0·37	—
Bureau Central Météorologique .	1893–4	1·6	0·16	0·76	0·40	0·57	2·01
Bureau Central Météorologique .	1894–9	1·4	0·21	0·57	0·56	0·50	1·53
Kew	1845–8	—	0·09	0·30	0·49	0·68	1·27
,, ...	1862–4	1·0	0·54	0·59	0·92	0·62	1·75
,, ...	1880	1·3	0·35	0·75	0·64	0·54	2·58
,, ...	1898–1904	1·3	0·18	0·52	0·36	0·44	2·00
Greenwich	1890–3	1·8	0·17	0·80	0·45	0·28	2·54

§ 12. Chauveau also analyses the several sets of data for the diurnal inequalities at the Bureau Central and the Eiffel Tower in Fourier series. He takes five terms, one more than I have taken for Kew, and says that the additional, or 4·8-hour term, distinctly improves the agreement with observation. I have expressed CHAUVEAU's values for the amplitudes in terms of the corresponding mean values of P taken as unity, and have calculated corresponding results for Kew from EVERETT's data as well as my own. In the latter case the values assigned to "summer" and "winter" are derived from the seasonal data at the foot of Table V., making use of the mean values of P given in Table I. For September and October I have taken the arithmetic means of the c's and α's for the two months. It seemed hardly worth while analysing a mean diurnal inequality from the two months combined, though that would have been more strictly correct. In the case of EVERETT's data the values refer in each case to a mean diurnal inequality for the period stated. Table VIII. gives the values thus found for the amplitudes, and Table IX. applies similarly to the phase angles. In this table the Kew angles have been modified so as to answer to local solar time, so as to be strictly parallel to CHAUVEAU's angles.

TABLE VIII.—Diurnal Inequality. Comparison of Amplitudes.

	Winter.				September and October.				Summer.			
	c_1.	c_2.	c_3.	c_4.	c_1.	c_2.	c_3.	c_4.	c_1.	c_2.	c_3.	c_4.
Kew, 1862–4	0·283	0·160	—	—	0·284	0·207	—	—	0·127	0·229	—	—
Kew, 1898–1904	0·102	0·103	0·033	0·010	0·060	0·190	0·033	0·025	0·079	0·213	0·021	0·027
Bureau Central, 1893	—	—	—	—	—	—	—	—	0·223	0·203	0·072	0·084
Bureau Central, 1894–8	0·220	0·104	0·035	0·031	0·144	0·211	0·060	0·055	0·130	0·200	0·040	0·068
Eiffel Tower, 1893	—	—	—	—	—	—	—	—	0·188	0·044	0·003	0·028
Eiffel Tower, 1896–8	—	—	—	—	0·157	0·036	0·007	0·015	0·133	0·085	0·023	0·021

TABLE IX.—Diurnal Inequality. Comparison of Phase Angles.

	Winter.				September and October.				Summer.			
	α_1.	α_2.	α_3.	α_4.	α_1.	α_2.	α_3.	α_4.	α_1.	α_2.	α_3.	α_4.
	°	°	°	°	°	°	°	°	°	°	°	°
Kew, 1862–4	184	193	—	—	170	189	—	—	111	179	—	—
„ 1898–1904	206	180	23	239	171	198	11	301	87	186	116	304
Bureau Central, 1893	—	—	—	—	—	—	—	—	96	200	190	8
„ 1894–8	223	206	45	0	182	213	358	11	95	197	157	352
Eiffel Tower, 1893	—	—	—	—	—	—	—	—	196	207	114	25
„ 1896–8	—	—	—	—	212	185	122	331	216	171	79	330

§ 13. It will be convenient to discuss the two tables together, and it must be remembered that amplitude now means the ratio borne by the actual amplitude of the periodic term to the mean value of the element during the day.

Comparing corresponding results from the Bureau Central and the Eiffel Tower, we infer that the amplitude of the 24-hour term varies but little, if at all, with moderate changes of height above the ground. Its value, however, at both places was much lower in the later series of years than in 1893. CHAUVEAU seems disposed to attribute this diminution to the fact that the efflux tube had been shortened, the reduction in the amplitude representing the increased disturbing influence of the building and other surroundings. A similar phenomenon, however, is seen at Kew in comparing the older and more recent data, and in an enhanced degree especially in winter and autumn, and at Kew the efflux tube was a foot *longer* in the later period than in the earlier. The phase angles in the 24-hour term at Kew and the Bureau Central both vary largely with the season, but are fairly similar at corresponding seasons, and the values from the earlier and later series of years are in fairly close agreement, notwithstanding the great differences in the amplitudes. On the other hand, the similarity in amplitude at the Bureau Central and the Eiffel Tower is accompanied by a large difference in phase, at least in summer. CHAUVEAU infers, from the similarity of the summer and autumn values of α_1 at the Eiffel Tower to the winter value at the Bureau Central, that the large seasonal change in α_1 at the latter station is a phenomenon confined to the lowest strata of the atmosphere. Experimental evidence is, however, necessary to justify the acceptance of this conclusion.

The 12-hour term shows very different phenomena. The amplitude apparently diminishes rapidly with the height, while the phase is comparatively little affected. Further, the phase angle at the Bureau Central, as at Kew, varies but little with the season, while both amplitude and phase angle vary but little with the epoch from which the data are derived. The phase angles at Kew and the Bureau Central do not differ much, but the angles at the former station appear consistently the smaller. The maxima at Kew are thus somewhat later in the day than at the Bureau Central, the difference in time from the mean of the three seasons in the latest sets of data being about half an hour.

§ 14. In consequence apparently of the rapid diminution in its amplitude with height CHAUVEAU seems disposed to regard the 12-hour term as of subsidiary importance, and due to special conditions in the very lowest strata, if not to purely local causes. A somewhat similar view has been expressed by Professor F. EXNER,[*] who bases his conclusions largely on observations he has made in the tropics. At some places, *e.g.*, in Ceylon, he seems to have found but little trace of the ordinary double maximum and minimum in the diurnal inequality. EXNER attributes the double maximum and minimum to a thin atmospheric layer near the ground, which exerts, he says, at some stations a large effect in the early afternoon hours through absorbing the sun's radiation of shortest wave-length. This absorbent stratum he believes especially characteristic of arid and dusty regions, while comparatively non-existent in moist climates, or where foliage is luxuriant. The conditions at Kew—a station situated in an extensive grass-covered park—are hardly such as EXNER associates with a large 12-hour wave. It is possible, of course, that the large extension of London since 1864 may have profoundly altered the electrical conditions even as far west as Kew; but if so, one would expect an enormous difference to manifest itself when the direction of the wind changes from east to west. I am not prepared to say that such a change of direction is wholly without effect—as it is difficult to distinguish between the direct effect of change of wind direction and the indirect effect of the change of weather conditions accompanying it—but if it exists it is by no means conspicuous. Also the difference between the earlier and later Kew data is not an increase in the 12-hour wave, but a diminution in the 24-hour wave. Faulty conditions or local peculiarities seem *a priori* more likely to introduce or enhance fictitious waves than to wipe out real periodic terms. The observed 24-hour wave, it must be remembered, shows a phase angle which varies largely with the season of the year, but the differences between the phase angles observed in 1862–4 and 1898–1904 are in most months comparatively small. If, then, the reduction in the amplitude apparent in the later series is due to some disturbing cause, that cause must have itself a phase which nearly keeps step with that of the real 24-hour potential wave throughout the year.

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[*] *Cf.* 'Terrestrial Magnetism,' vol. 7, 1902, p. 89.

Before attaching much importance to views which after all are mainly theoretical, it should be remembered that the older Kew data refer to *all* days, the later only to *fair weather* conditions. Future investigations may show the 24-hour term to be more dependent on the meteorological conditions than the 12-hour term. Also in considering the relative importance of the two terms we should make allowance for the fact that it is the conditions close to the ground that are at present of most immediate practical importance both to human beings and to agriculture.

§ 15. Returning to the consideration of Tables VIII. and IX., it will be seen that with the exception of the values of α_4 in winter—when the amplitude at Kew was so small that considerable uncertainty must exist—the Kew and Bureau Central values of α_3 and α_4 are sufficiently close to raise a strong presumption that the 8- and 6-hour terms represent a true atmospheric electricity effect. The comparative agreement between the phase angles from the earlier and later series of observations at the Bureau Central and the Eiffel Tower favour the same conclusion.

The 8- and 6-hour waves are decidedly smaller at Kew than at the Bureau Central. The difference in this case may not improbably be partly due to greater homogeneity in the Kew data. The fact that the 8- and 6-hour terms are also much less at the Eiffel Tower than at the Bureau Central must, however, have some other explanation; it is most natural to ascribe it to the influence of height.

Irregular Diurnal Changes.

§ 16. Hitherto we have exclusively considered the regular diurnal changes, those for each month being derived by taking hourly means from about 70 days and eliminating any non-cyclic element. The amplitude of these periodic changes gives, however, a very inadequate idea of the phenomena. Even in the finest weather the regular diurnal change is accompanied by numerous irregular changes, and very often the latter so predominate that the former is but inconspicuously shown in the photographic trace. I have thus gone into the individual day's results with some minuteness. My object was chiefly to ascertain the effect of different meteorological conditions—a subject considered later—but also partly to see whether any sort of proportionality existed between the size of the regular and irregular movements throughout the year. The results of this latter investigation are summarised in Table X.

TABLE X.—Results from Individual Days.

	Mean of maximum and minimum.	Range.	Non-cyclic change. ±	Ratios to mean value for the 24 hours.			Ratio of the mean of individual daily ranges to the range in the diurnal inequality.
				Mean of maximum and minimum.	Range.	Non-cyclic change. ±	
January . . .	212	203	93	1·05	1·01	0·46	2·79
February . .	234	218	86	1·05	0·98	0·39	2·32
March . . .	197	210	85	1·10	1·17	0·47	2·52
April	153	164	62	1·11	1·19	0·45	2·22
May	135	143	53	1·10	1·17	0·44	2·03
June	120	132	45	1·09	1·19	0·41	2·33
July	109	117	40	1·12	1·20	0·41	2·12
August . . .	123	129	41	1·08	1·13	0·36	2·17
September . .	129	141	54	1·07	1·16	0·45	2·61
October . . .	163	196	80	1·06	1·28	0·52	3·13
November . .	206	186	74	1·03	0·93	0·37	3·60
December . .	247	213	96	1·02	0·88	0·40	2·59
Year	169	171	67·5	1·071	1·107	0·426	2·54
Winter . . .	225	205	87·2	1·037	0·949	0·403	2·83
Equinox . . .	161	178	70·4	1·083	1·200	0·473	2·62
Summer . . .	122	130	44·9	1·094	1·173	0·403	2·16

The first numerical column of Table X. gives the monthly and seasonal mean values of the arithmetic mean of the largest and smallest hourly values in individual days; the fourth column shows the ratio which the value thus found for the month or season bears to the corresponding mean value of P.

The second column gives the monthly and seasonal mean values of the excess of the largest over the smallest hourly value in individual days, the non-cyclic effect *not* being eliminated. The fifth column shows the ratio borne by the mean range thus found for the month or season to the corresponding mean value of P.

The third and sixth columns similarly relate to the non-cyclic effects treated *numerically.*

The unit in the first three columns is, as in Tables I. to VI., 1 volt per metre.

The last column gives the ratios borne by the ranges in the second column to the corresponding amplitudes of the regular diurnal inequality as given in Table III.

The monthly means in the first three columns of Table X. were really calculated to one significant figure beyond that recorded, and these more exact results were employed in deducing the seasonal means and the ratios.

Several interesting and novel results appear.

The mean of the largest and smallest hourly values exceeds in every case the true mean from the 24 hours; but the excess is not large, and, though slightly less in winter than in the other seasons, varies comparatively little throughout the year.

The mean of the individual daily ranges is, on the average, no less than $2\frac{1}{2}$ times the amplitude of the regular diurnal inequality.

The ratio borne by the irregular to the regular range is distinctly greater in the winter and equinoctial than in the summer months, showing a fairly well marked maximum in October and November.

Taking the year as a whole, the mean of the individual daily ranges exceeds the mean value of P by about 10 per cent.—a somewhat remarkable fact; the ratio borne by the former quantity to the latter falls slightly below unity in three of the winter months, but seems nearly uniform from March to September.

The (numerical) non-cyclic effect resembles the mean of the individual daily ranges in being largest, absolutely considered, in winter, while showing the largest ratio to the mean value of P in the equinoctial season. The large size of the average non-cyclic effect, when taken independent of sign, is an important element in determining the significance to be attached to the results obtained in Table II. where it is treated algebraically.

Special Meteorological Features of the Selected Days.

§ 17. In confining ourselves to 10 selected days a month we have followed a precedent set by the annual selection of 5 magnetically "quiet" days a month by the Astronomer Royal. In the case of the magnetically quiet days, so far as is known at present, there is no systematic departure from average conditions in anything but the phenomena of Terrestrial Magnetism. In the present case, however, it is otherwise. We have eliminated all the rainy days, which constitute a considerable proportion of the days in most winter months, and not infrequently even in summer months. The meteorological conditions on the average selected day thus represent a climate which at some seasons of some years is far from being representative of Kew. It seemed important to ascertain what this difference really amounted to. Fortunately, Kew is a first order meteorological station, so that exceptionally full information is available as to the hourly and the mean daily and monthly values of the meteorological elements.

A comparison was accordingly instituted between mean values deduced for each month from the 10 selected days and the corresponding published means taken from all days of the month. This was done for the mean barometric pressure of the day, the mean temperature, the mean hourly wind velocity, and the daily record of bright sunshine. All these elements are recorded directly by self-recording instruments of high accuracy, and the pressure and temperature daily means are based on hourly readings. The means from all days of the month are regularly calculated and recorded by the Meteorological Office; the means from the selected days were specially calculated by members of the Observatory staff.

The results of the comparison appear in Table XI.

It is at once apparent that the 10 selected days represent a climate having more sunshine and a higher barometer than Kew, but which has a distinctly lower winter temperature, and in most months of the year appreciably less wind. In summer the temperature of the selected days is, if anything, slightly above the normal, but the difference is too small to rely on. Absolutely considered, the difference as regards sunshine is largest in summer; but relative to the average amount actually experienced the difference is really greater in winter.

TABLE XI.—Mean Excess of Element on the 10 Selected Days as compared to All Days of the Month.

	Barometric pressure (inches).	Temperature, Fahrenheit.	Wind run, miles per hour.	Sunshine, hours per day.
		°		
January	+0·132	−2·98	−1·98	+1·02
February	−0·001	−1·70	−2·28	+0·33
March	+0·083	−0·98	−1·93	+0·38
April	+0·090	−0·79	−1·30	+1·75
May	+0·096	−0·14	−1·09	+1·79
June	+0·068	+0·17	−0·09	+1·40
July	+0·010	+0·50	+0·12	+0·96
August	+0·055	−0·01	−0·48	+1·36
September	+0·017	+0·40	−0·78	+1·13
October	+0·042	−1·12	+0·79	+0·95
November	+0·101	−2·35	−0·91	+0·12
December	+0·101	−3·08	−3·21	+0·02
Year	+0·066	−1·01	−1·10	+0·93
Winter	+0·083	−2·53	−2·10	+0·37
Equinox	+0·058	−0·62	−0·80	+1·05
Summer	+0·057	+0·13	−0·39	+1·38

Connection of Atmospheric Potential with Meteorological Elements.

§ 18. There are so many possible ways in which a connection may subsist between electric potential and a meteorological element that it is difficult to know how to attack the problem. Suppose, for instance, that a particular June had a very high mean temperature, then there might be an effect either on the mean value of P, or on the amplitude of the daily changes, or on both. Possibly, however, there might be no appreciable effect on either quantity, and yet an appreciable difference might exist between the electric phenomena of the hotter and colder days of the average June. The former phenomenon would usually be interpreted to mean that no direct connection exists between potential gradient and temperature; the latter would naturally be interpreted in the opposite sense; and yet neither interpretation would be justifiable without further investigation. A very warm June would differ from the average June in other respects besides temperature, and a true direct temperature effect might be practically annulled by some other effect. Again, during an ordinary June, a hot and a cold day usually present notable differences in other meteorological elements besides temperature.

The first method I have applied is to divide the 7 Januarys, 7 Februarys, and so on, into two groups, one of three the other of four, according to the size of the mean potential gradient, and to find the difference between the meteorological elements for these two groups, taking first the selected days only, and then all the days of the month. The sub-division of each seven months was done from consideration of the mean potential only, the choice being decided by whether the biggest gap in the values of P occurred between the third and fourth, or between the fourth and fifth on the list, when the months were arranged in the order of the size of P. It is necessary to deal with the months of the year separately. The combination of days from all seasons of the year inevitably leads to error. The cold days, for instance, then come mainly from winter, and the hot days from summer, and the effects of the regular annual variation get mixed up with any true temperature effect.

Table XII. gives the results of the comparison; *s* stands for the mean from the selected days only, *a* for that from all days of the month. The excess is shown for P as well as for the meteorological elements, as the size of the potential difference should be taken into account in considering the part that chance may play in the results.

TABLE XII.—Mean Excess of Values of Meteorological Elements for Group of Years of Larger as compared to Group of Smaller Potential Gradient from *s* (selected days) and *a* (all days of month).

	Potential gradient.	Barometric pressure, in inches.		Temperature, Fahrenheit.		Wind, miles per hour.		Sunshine, hours per day.	
		s.	*a*.	*s*.	*a*.	*s*.	*a*.	*s*.	*a*.
January	67	−0·061	−0·058	−1·1	−1·1	+0·1	+1·2	−0·15	+0·10
February	73	+0·015	+0·064	−0·9	−2·5	−1·2	−3·0	−0·32	−0·03
March	40	+0·023	+0·042	+1·1	+0·8	+2·1	+0·8	+1·61	+1·01
April	34	−0·059	+0·033	−3·3	−0·6	+4·5	+1·2	−1·58	−0·61
May	49	+0·076	+0·057	+0·4	+2·0	−0·3	−0·1	+2·32	+0·99
June	31	+0·031	−0·014	−0·4	−1·3	+1·3	+0·1	+0·59	+0·04
July	20	0·000	0·000	−2·0	−1·9	+1·3	+0·7	−0·27	−0·88
August	22	−0·021	+0·005	+2·5	+2·0	+2·7	+2·0	+0·34	+0·76
September	37	+0·037	+0·071	+2·2	+0·4	+0·1	+0·6	+1·36	+0·70
October	40	+0·041	+0·015	−1·8	−0·4	−2·4	−1·5	−0·31	−0·17
November	72	−0·016	+0·062	−1·7	−3·2	−2·7	−1·5	+0·13	+0·13
December	84	−0·146	−0·047	−1·9	−1·4	−2·0	−1·7	−0·39	−0·44
Year	47	−0·006	+0·019	−0·58	−0·60	+0·29	−0·10	+0·28	+0·13
Winter	74	−0·052	+0·005	−1·40	−2·05	−1·45	−1·25	−0·18	−0·06
Equinox	38	+0·011	+0·040	−0·45	+0·05	+1·08	+0·28	+0·27	+0·23
Summer	30	+0·022	+0·012	+0·12	+0·20	+1·25	+0·68	+0·74	+0·23

The difference between the mean values of P for the two groups is considerably larger in winter than in summer, but in every case it represents a very appreciable fraction of the mean from the whole 7 years. As a rule, the meteorological results have the same sign whether we take all the days of the month or the selected days only.

In the four summer months there seems an association of high potential with high barometer, high temperature, high wind velocity and much sunshine; but the association with temperature in particular is very doubtful, two months going one way and two the other. Equinox agrees on the whole with summer, but the association is less clear. In winter the results seem the exact opposite of those in summer, but the association with sunshine is small and uncertain.

The association of high potential with low temperature in winter is the most consistent. It will be remembered that the selected days in winter show a markedly lower temperature and less wind velocity than the average day of the month, and these meteorological conditions, as we now see from Table XII., appear to be associated at that season with large values of P.

§ 19. The second method adopted was to split the ten selected days in each individual month into two groups of 5, the one containing the days of highest mean P, the other those of lowest mean P. In the case of March, for instance, we thus split

70 days into two groups, to the one of which each year contributes the five days in which P was greatest, while to the other it contributes the five days in which P was least. Table XIII. shows the excess of the mean P in the former group and of the corresponding mean values of certain meteorological elements as compared to the means from the second group.

This second method gives notably larger differences of potential between the two groups, and so is more likely *a priori* to present decisive results than Table XII. In Table XIII. there seems in winter a very distinct association of high potential with low temperature and with low wind velocity. This is so far in accordance with Table XII.; but the association of high potential with low temperature in Table XIII. extends to every month of the year except July, whereas in Table XII. March, May, August and September are exceptions to the rule.

TABLE XIII.—Mean Excess of Values of Meteorological Elements for Groups of Days of Larger as compared to Groups of Days of Smaller Potential Gradient.

	Potential gradient.	Barometric pressure in inches.	Temperature, Fahrenheit.	Wind, miles per hour.	Sunshine, hours per day.
			°		
January	128	+0·191	−5·09	−3·33	+0·40
February	109	−0·009	−5·99	−3·22	+1·26
March	89	+0·021	−2·88	−1·40	+1·26
April	73	+0·006	−2·94	−2·62	−0·59
May	59	+0·009	−4·72	+0·04	−0·53
June	52	−0·009	−1·40	+2·07	−0·26
July	45	+0·008	+1·94	−0·26	+2·65
August	47	−0·006	−0·81	−0·63	+0·81
September	50	−0·023	−2·71	+0·45	+0·43
October	81	−0·058	−3·28	+1·11	+0·91
November	115	+0·109	−5·49	−2·13	+0·79
December	130	+0·054	−6·22	−0·64	+0·05
Year	81	+0·024	−3·30	−0·88	+0·60
Winter	120	+0·086	−5·70	−2·33	+0·62
Equinox	73	−0·014	−2·95	−0·62	+0·50
Summer	51	0·000	−1·25	+0·30	+0·67

Table XIII. shows also a greater apparent association of high potential with much sunshine than does Table XII.

As regards barometric pressure, Table XIII. shows from April to August almost no trace of any association with potential gradient, and the results for the six months, September to February, in Tables XII. and XIII. differ in sign even. The results for barometric pressure are thus exceedingly contradictory.

§ 20. The months which show a high mean value of P show also a large average daily range, but it by no means follows that the causes to which the two phenomena are due are the same. I thus split the 10 days of each month into two groups, according to the size of the potential range, and have compared the mean results from the two groups of 35 days derived in this way from the seven years. Except as regards the criterion by which the 10 days were subdivided, the procedure was exactly the same as that followed in calculating Table XIII. The results of the new subdivision are shown in Table XIV.

TABLE XIV.—Mean Excess of Values of Meteorological Elements for Groups of Days of Larger as compared to Groups of Days of Smaller Potential Range.

	Potential range.	Barometric pressure in inches.	Temperature, Fahrenheit. °	Wind, miles per hour.	Sunshine, hours per day.
January	116	+0·194	−2·14	−1·39	+0·54
February	104	+0·027	−2·35	−1·35	+1·15
March	113	+0·012	−2·33	−1·74	+1·23
April	87	+0·036	−2·78	−2·74	−0·41
May	83	−0·072	−3·98	+0·33	−1·27
June	66	−0·048	0·00	+2·30	+0·05
July	71	−0·022	+2·22	+0·02	+2·12
August	62	0·000	−0·29	−1·02	−0·37
September	57	+0·001	−1·59	−0·30	−0·61
October	117	−0·013	−1·93	+1·13	+0·50
November	113	+0·094	−3·58	−1·71	−0·21
December	113	+0·150	−3·88	−0·08	+0·14
Year	92	+0·030	−1·89	−0·55	+0·24
Winter	112	+0·116	−2·99	−1·13	+0·40
Equinox	94	+0·009	−2·16	−0·91	+0·18
Summer	70	−0·035	−0·51	+0·41	+0·13

Comparing Tables XIII. and XIV., we find that the signs of the meteorological differences agree in the large majority of instances. The meteorological conditions which are associated with high potential thus appear associated with a large diurnal range. The phenomenon may mean nothing more than that the size of the daily range tends *ceteris paribus* to increase or diminish according as the mean value of P is greater or less. The association, however, with low temperature, low wind velocity, and long sunshine, seems decidedly less in Table XIV. than in Table XIII. There is considerably greater regularity in the results for barometric pressure in Table XIV. than Table XIII., but the relationship with P seems decidedly opposite in summer to what it is in winter. The natural inference is that there is little if any *direct* connection between the absolute height of the barometer and the size of either the daily mean or the irregular daily range of P. On the other hand, in winter it seems clear that the weather conditions which accompany a high barometer favour the existence of high values and big diurnal changes in P.

TABLE XV.

	Excess from groups of days of highest barometric pressure.					Excess from groups of days of highest temperature.				
	Barometric pressure in inches.	Mean potential.	Potential range.	Non-cyclic effect.		Temperature, Fahrenheit.	Mean potential.	Potential range.	Non-cyclic effect.	
				Algebraic.	Numerical.				Algebraic.	Numerical.
						°				
December .	+0·447	+36	+52	+ 2	+51	+8·17	−108	−46	+ 6	−29
January .	+0·540	+59	+10	+ 4	+ 4	+7·76	− 80	+ 1	+39	−21
June. . .	+0·204	+ 6	− 7	+13	− 7	+7·04	− 18	−20	− 2	−18
July. . .	+0·205	− 2	− 7	+16	0	+7·15	+ 6	+11	+ 2	−11
August . .	+0·252	+13	+11	+31	+ 9	+5·44	− 10	− 9	−12	+ 5

§ 21. Instead of the mean value of P, or of the range of P, one may take for the criterion in grouping the selected days the value of some one meteorological element. This is a delicate mode of analysis, so far as the particular element is concerned; but to carry it out for each element, for each month of the year, would have involved a very serious amount of arithmetic. The method has thus been applied only to some of the elements, and only for a selection of months.

Table XV. gives the results thus found in the case of mean barometric pressure and mean daily temperature. December and January were selected as the months when according to Tables XIII. and XIV. the most decisive results might be expected. June, July and August were selected partly as representing summer, and partly in consequence of the exceptional nature of the July results in Tables XIII. and XIV. There appears in Table XV., as in the tables just mentioned, a decided association of high potential and large range with high barometer in December and January. In summer the range of barometric pressure is much less, so we should not in any case expect the effects on the potential to be so conspicuous. The results, however, are not merely smaller numerically in the three summer months, but they differ in sign amongst themselves. Table XV. thus agrees with Tables XIII. and XIV. in pointing to the conclusion that any association of mean potential or potential range with barometric pressure in summer is small and doubtful. In all five months there is in Table XV. an apparent tendency for P to increase more (or diminish less) throughout the 24 hours when pressure is high than when it is low; curiously, however, this effect seems much larger in the summer than in the winter months. The exceptionally large size of the non-cyclic effect, when taken irrespective of sign, in December when pressure is high, and the correspondingly large size of the range, are both probably due in considerable measure to fog. This is an element whose intensity at two consecutive midnights is usually widely different.

In the case of temperature, July stands out from the other months exactly as it did in Tables XIII. and XIV. The association of high temperature with low potential is again most conspicuous in the winter months.

Accompanying the diminished value of P we have a diminution in the non-cyclic effect treated numerically. The apparent absence of temperature effect on the potential range in January, and the exceptionally large tendency to an increase in P during days when temperature was high, are probably due to some common cause.

§ 22. If there were a direct causal connection between *any one* meteorological element and potential gradient or range, we ought to get the same or at least closely similar results for the ratio (difference of potential)/(difference of element) when the ratio is derived from a Table such as XV., and when it is derived from a Table such as XIII. or XIV. If such an influence though not unique were dominant, the two ratios so found should be at least of the same order. Combining the results from the two months, December and January, I find for the ratios of the differences—the units being for temperature 1°, for pressure 1 inch—

	$\frac{\text{Mean potential}}{\text{Temperature}}$.	$\frac{\text{Potential range}}{\text{Temperature}}$.	$\frac{\text{Mean potential}}{\text{Barometric pressure}}$.	$\frac{\text{Potential range}}{\text{Barometric pressure}}$.
By Table XV.	−12	− 3	+ 96	+ 63
„ Tables XIII. and XIV.. .	−23	−38	+1053	+666

The case of mean potential and temperature is the only one in which the ratios are of the same order.

The mean temperature of the selected days in December and January was 38°·3 F.

If instead of December and January we had taken June and August, we should have got altogether different results for the potential-temperature ratios, while taking July the sign even would have changed. Thus, if any direct relationship exists between potential and temperature, it must give a ratio between potential change and temperature change, which alters rapidly, and which changes sign at a temperature between 64°·5 (the mean temperature for the selected days in July) and 60°·3 (the mean temperature for the selected days of June and August).

It may be the purest accident, but somewhat similar ideas present themselves when we consider the mean seasonal values of potential and temperature. For these, taking the temperatures of the selected days, I find—

	Mean potential.	Mean temperature.
		°
Winter	217	39·2
Equinox.	148	48·8
Summer	111	59·3

For the ratio of (potential decrease)/(temperature increase) we have from—

	Winter and equinox.	Winter and summer.	Equinox and summer.
Ratio	7·2	5·3	3·5
Mean of temperatures . . .	44°·0	49°·2	54°·0

The values thus diminish markedly as the mean temperature alters. Further, for nearly equal increments in the mean temperatures we have nearly equal decrements in the ratio. Also, if the ratio were to diminish at the same rate as the mean temperature rose further, we should have it vanishing altogether below 64°, *i.e.*, below the mean temperature of the selected days in July.

§ 23. The only other meteorological element which I have investigated in the same way as pressure and temperature is the duration of sunshine. Several authorities, *e.g.*, ELSTER and GEITEL at one time, have regarded ultra-violet radiation from the sun as probably a most important agent in the phenomena of atmospheric electricity. If this were the case, one would expect to find a conspicuous difference in summer between days of much and of little sunshine. The grouping of the days according to sunshine in the way described above led to the following results for the excesses in the groups of days of most sunshine :—

TABLE XVI.

	Sunshine, hours per day.	Mean potential.	Potential range.	Non-cyclic effect.	
				Algebraic.	Numerical.
June	7·2	− 9	− 4	−27	+2
July	6·7	+23	+28	+ 9	+2
August	6·0	+ 7	− 8	+14	−4

If the July data alone existed, then the conclusion one would naturally draw from the above figures—just as from the corresponding figures in Tables XIII. and XIV.—is, that with long duration of sunshine there is a very appreciable rise both in the mean potential and in its daily range. If June and August however are combined, we get for practically the same excess in hours of sunshine a wholly negligible effect on the value of the mean potential; whilst the apparent effect on the range, such as it is, is opposite in sign to that observed in July.

§ 24. The effects of temperature, barometric pressure, wind and sunshine on the simultaneous values of the potential gradient at Kew were also considered in my previous paper* of 1896, which dealt however only with eye observations at one or two hours during some months of 1895 and 1896. The results obtained are generally similar, except that in 1896 I found an apparent association of low potential with long previous sunshine. Even here the contradiction may be more apparent than real, as the influence of sunshine may depend on the hour of the day. An intensification for instance of the afternoon minimum may be accompanied by a compensating increase of potential during the night. Considerations of this kind must in fact be borne in mind in other cases besides that of sunshine.

§ 25. In 1896 I paid special attention to aqueous vapour, as EXNER's theory, which associated potential gradient and aqueous vapour in a definite formula, was then rather in the ascendant. I advanced grounds—whose cogency will now, I think, be hardly questioned—for believing the theory in its general form to be untenable. The 1895–6 data were from a Kelvin portable electrometer, whose insulation was never in doubt. The present data are from an electrograph, whose insulation may depend, especially at night—sometimes it may be feared not inappreciably—on the greater or less dryness of the air. Also, for one and the same amount of aqueous vapour in the air, it seems all important so far as potential is concerned whether fog forms or not, and in the long nights of winter no satisfactory data exist as to the occurrence of fog, or its thickness when present. I have thus omitted consideration of the effects of aqueous vapour as too large a subject to be included in the present paper.

A similar remark applies to wind direction. There are here two main difficulties: first the fact that the direction is perpetually shifting, and the extent of the variation in a single day is often large; second the fact that when the wind is light—and there are few fine weather days when this does not happen sometime during the 24 hours—the record of direction is often uncertain, the strength of the wind being insufficient to turn the vane of the Robinson cup anemograph. In particular is this true of foggy days in winter, the precise days in which the potential tends to be highest.

APPENDIX.

On the Relation between the Regular Diurnal Changes of Barometric Pressure and Potential Gradient.

§ 26. The only meteorological element whose diurnal inequality presents two prominent maxima and minima is the barometric pressure. EVERETT seems to have been the first to call attention to the similarity between the regular diurnal inequalities of potential and barometric pressure, and the potential data which he considered more especially in this connection were those from Kew. Having no Kew barometric data, EVERETT employed instead some from Halle. Confining himself to the mean

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[*] *Loc. cit.* (for summary of results, see pp. 130, 131).

diurnal inequalities for the year, he found that "the barometric curve for Halle bears a strong resemblance to the Kew electrical curve, but is upwards of an hour later in phase." Several other writers have since called attention to general resemblances of this kind. Of late years, additional interest has attached to the possibility of the connection, owing to ELSTER and GEITEL's discovery that air drawn from the soil is ionized, and their consequent suggestion that change of barometric pressure may influence potential gradient, by modifying the rate at which this ionized air escapes into the atmosphere.

The diurnal inequality of barometric pressure is an element considerably dependent on local conditions, and it thus appeared essential to an adequate discussion to have barometric data for Kew. Diurnal inequalities were accordingly got out by the Observatory staff for each month of the year for an 11-year period 1890 to 1900, making use of the data published by the Meteorological Office in the 'Hourly Means.'

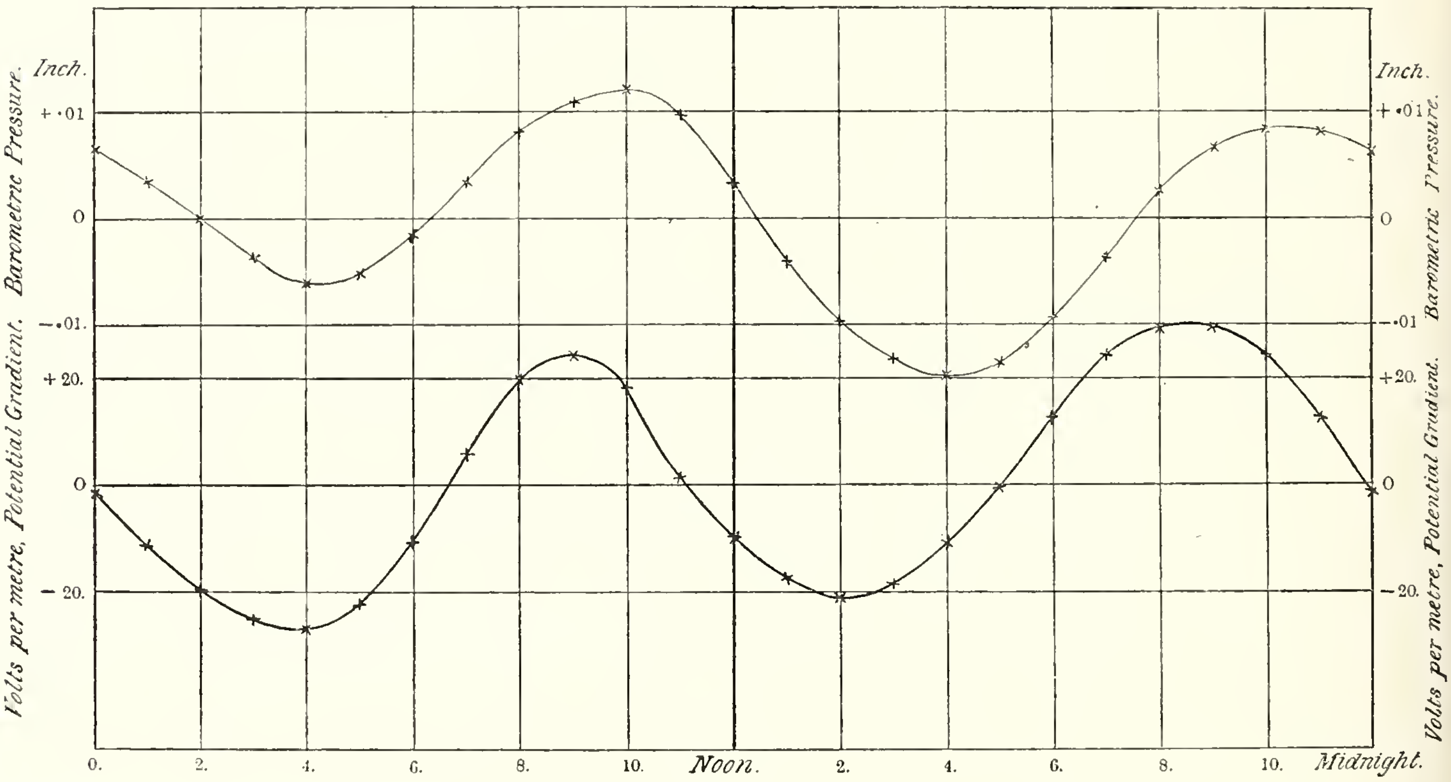

Fig. 4.

The *regular* diurnal change is a small quantity, and accordingly means were calculated to 0·0001 inch This is perfectly legitimate, as the curves are read to 0·001 inch, and each hourly value in the mean diurnal inequality for a month was based on over 300 individual readings. For our present purpose full details of the diurnal inequalities are not absolutely necessary, and I have consequently omitted them to economise space.

§ 27. That EVERETT had a substantial basis in claiming a resemblance between the mean diurnal inequalities for the year in barometric pressure and potential gradient is apparent on comparing the two curves of fig. 4. The heavy curve, representing potential gradient, is drawn on a more open scale than the curves of fig. 2; the light curve representing barometric pressure is drawn on a scale such as to make its apparent range nearly equal to that of the other curve.

Whilst the resemblance is very striking, as between two different elements, there are differences which seem of a fundamental character. During the forenoon the curves are nearly in the same phase. The barometer curve lags a little, but very little, behind the other. In the afternoon, however, the lag in the barometer curve becomes conspicuous, amounting to about two hours at the times of the afternoon maximum and minimum.

This change in apparent lag throughout the day does not seem to have been noticed previously, but it persists with wonderful regularity throughout the year. Treating the maxima and minima as occurring *at the exact hours* when the algebraically greatest and least hourly values occur, I find that the hour of the forenoon minimum is the same for the two elements in every month from January to October; the mean lag for the barometric pressure for the 12 months comes to $\frac{5}{12}$ of an hour, but the exceptionally early hour of the potential minimum in October is responsible for more than half this difference.

In the case of the forenoon maximum there is exact agreement in the hour in eight months, and the mean lag in barometric pressure for the 12 months is only $\frac{1}{3}$ hour.

December is the only month when the afternoon minima accord in time, and the mean lag for the barometric pressure is $1\frac{1}{2}$ hours. The corresponding quantity for the afternoon maxima is $2\frac{1}{3}$ hours.

If the relation is a case of cause and effect, the fact that it is the barometer curve that lags relative to the other would naturally lead one to regard the potential variation rather as the cause than the effect.

§ 28. When we consider the variation from month to month in the amplitudes of the diurnal inequalities other differences appear. This will be seen on comparing Table XVII. with Tables III. and IV. The first column in Table XVII. gives the range, or difference between greatest and least hourly values, in the diurnal inequality of barometric pressure; the second column the numerical sum of the 24 hourly differences from the mean for the day. The corresponding potential quantities will be found in the two last columns of Table III. The ranges and the sum of the differences show analogous phenomena, but the latter are the better for comparison, because they give a smoother annual variation when the number of years considered is limited.

Comparing, then, the second column of Table XVII. and the last column of Table III., we see that in B (barometric pressure) the values for the winter months November to February are decidedly the least, and the values for April, May, June, and September the largest. In P (potential gradient), on the other hand, the largest values occur in December, February, and March, and these are much in excess of the

TABLE XVII.—Barometric Pressure. Diurnal Inequality (Unit 0·0001 inch).

	Range.	Sum of 24 differences.	Day fall.	Night fall.
January	280	1655	280	187
February	262	1657	262	176
March	298	1840	298	166
April	320	2101	320	166
May	339	2157	328	138
June	307	1933	307	128
July	282	1747	268	157
August	328	1852	328	93
September	345	2052	345	151
October	250	1822	250	210
November	284	1561	284	147
December	295	1649	295	188
Arithmetic mean	299	1835	297	159
From mean diurnal inequality for year	268	1699	268	152

values in the summer months. The annual variations in the sum of the differences for B and P are shown together in fig. 1. To get a smooth curve in either case would probably require some 30 years' observations, but the differences between the two curves speak for themselves.

§ 29. Whilst the difference of phase in the two curves of fig. 4 is what most readily catches the eye, another difference seems not less important. In the P curve the afternoon maximum and the morning minimum are respectively the largest and smallest values in the day; but in the B curve it is the morning maximum and afternoon minimum that are the extremes.

Comparing the two last columns in Table XVII. with the day and night falls of P in Table IV. we note again an essential difference. In the case of B the day fall is the larger in every month of the year. The excess, it is true, is most conspicuous in summer (the season when the day fall in P exceeds the night fall), but taking an arithmetic mean from the four winter months, November to February, we have

$$\text{day fall} / \text{night fall} = 1{\cdot}6 \quad \text{in B},$$

$$= 0{\cdot}55 \text{ in P}.$$

§ 30. To disclose more exactly the nature of the differences, the monthly and seasonal diurnal inequalities of barometric pressure were analysed in Fourier series with 24, 12, 8, and 6-hour terms. The results appear in Table XVIII., the notation used corresponding exactly to that of Table V.

TABLE XVIII.—Barometric Pressure, Diurnal Inequality, Amplitudes, and Phase Angles (Unit for Amplitudes, 0·0001 inch).

	c_1.	α_1.	c_2.	α_2.	c_3.	α_3.	c_4.	α_4.
		° ′		° ′		° ′		° ′
January . .	5·1	199 28	99·3	153 59	49·3	345 38	22·5	210 55
February .	8·6	44 37	104·8	150 12	31·4	342 53	9·8	91 42
March . .	40·0	28 18	115·8	150 13	18·1	332 33	13·4	24 25
April. . .	82·2	30 7	117·9	151 26	9·4	170 42	11·7	− 8 46
May . . .	108·9	29 41	103·3	148 39	23·5	160 38	5·4	−44 46
June . . .	93·0	16 13	91·7	144 6	29·5	160 44	1·1	−62 1
July . . .	67·0	18 12	94·0	140 20	31·6	151 4	2·6	−51 31
August . .	94·8	6 45	92·3	140 43	13·7	156 16	15·6	−50 18
September .	72·5	5 19	122·3	151 32	2·3	352 45	10·7	−20 42
October . .	13·9	115 23	113·6	158 28	28·6	357 18	5·9	17 16
November .	13·6	317 32	99·7	158 10	38·8	354 51	10·1	189 1
December .	18·1	83 35	98·2	151 57	46·3	351 34	22·7	216 1
Year . . .	47·1	21 12	103·9	150 15	9·1	359 0	2·9	282 27
Winter . .	4·7	44 29	100·3	153 32	41·3	348 55	12·7	199 14
Equinox. .	47·5	24 44	117·2	152 52	9·6	347 17	9·9	2 30
Summer. .	89·9	18 8	95·2	143 35	24·5	156 58	6·1	310 15

Comparing Tables XVIII. and V., we see that in both the amplitude of the 24-hour term varies much with the season; but whereas in the case of P it is conspicuously largest in winter, that is precisely the season when it is least in B. Table XVIII. shows apparently a secondary minimum for c_1 in summer, but the smallest value in summer is 13 times the value in January. The fundamental nature of the difference between the annual variations of c_1 in B and P can in fact be seen at a glance on comparing the heavier and lighter full line curves in fig. 3, which represent the monthly values expressed as fractions of the arithmetic mean.

The phase angles α_1 in Table XVIII. show erratic variations in the winter months, which are very probably fictitious. Judging by the seasonal values, α_1 is larger in winter than in summer, but the difference is small compared to the corresponding difference in Table V. In all the seasons α_1 is much less for B than for P, in other words, the hour of maximum for P is much the earlier.

§ 31. In the case of the 12-hour term the differences between the annual variations in the amplitudes for B and P are comparatively small. These variations are illustrated by the dotted curves in fig. 3.

The phase angles α_2 in Table XVIII. show fairly similar characteristics to those exhibited in Table V. In both cases the seasonal variation is comparatively small. The P phase angle is invariable the larger, *i.e.*, the maxima in the 12-hour curve are again earlier for P than for B; the difference in time is however on the average only slightly over an hour, though greater in summer than in winter.

The 8-hour term in B is unusually large. In winter c_3 is in fact much in excess of c_1.

The annual variation of c_3 is regular and strongly developed, but is of a very unusual character. The winter and summer values of α_3 in Table XVIII. are nearly opposite in phase. There is also a considerable difference between the winter and summer values of α_3 in Table V., but the difference is twice as big for B as for P and is exactly in the opposite direction.

In the case of the 6-hour term the phase angles in B and P vary somewhat similarly with the season, and the difference in the case of the mean diurnal inequalities for the year represents a difference of only some 10 minutes in time. The annual variation of c_4 is somewhat irregular in both elements, and a long series of year's data would be necessary for a satisfactory comparison.

§ 32. When comparing the Kew data with those from the Bureau Central and the Eiffel Tower, we found that the 12-hour term in the diurnal inequality of potential was the only one which presented under all conditions closely similar features as regards times of maxima and minima, and as regards amplitude near the ground. Similarly, it is well known that the 12-hour term in the diurnal inequality of barometric pressure presents at the ground level phenomena of a much more regular character than does the 24-hour term. The latter term seems largely dependent on local conditions, whereas the 12-hour term is usually pretty much the same at places of nearly the same latitude. These phenomena are shown in a striking fashion by comparing the data of Table XVIII. with corresponding data for Jersey* based on observations by DECHEVRENS.

In view of these facts, it is highly significant that the general resemblance that has been noticed between the diurnal inequalities of potential gradient and barometric pressure is now found to proceed almost entirely from the parts that have a 12-hour period. At Kew, at least, so far as the 24-hour terms are concerned, it is a case not of resemblance, but of marked dissimilarity.

During the seven years whose data have been considered, the charge of the electrograph and the taking of the absolute observations have devolved upon Mr. E. G. CONSTABLE, the Senior Assistant engaged in the meteorological work of the Observatory Department, and his Junior Assistant, Mr. E. BOXALL. The selected days were chosen by Mr. CONSTABLE in consultation with myself.

The chief burden of the preliminary work was borne by Mr. CONSTABLE, who drew the free-hand pencil curves and took all the measurements. A good deal of the arithmetical work was done by other members of the staff, especially by Messrs. BADDERLY and FRANCIS. All the reductions and calculations have been carefully checked, mostly by myself, and notwithstanding the multiplicity of details I hope no serious errors remain undetected. It remains to express my thanks to the Meteorological Office—to whom the Electrograph belongs—and to the Director, Dr. SHAW, for permission to publish the results.

* 'Meteorologische Zeitschrift,' August, 1905, p. 384.

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[PLATES 1–8.]

GALVANIC CELLS PRODUCED BY THE ACTION OF LIGHT

THE CHEMICAL STATICS AND DYNAMICS OF REVERSIBLE AND IRREVERSIBLE SYSTEMS UNDER THE INFLUENCE OF LIGHT

(SECOND COMMUNICATION)

BY

MEYER WILDERMAN, PH.D., B.SC. (OXON).

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VII. *Galvanic Cells Produced by the Action of Light.—The Chemical Statics and Dynamics of Reversible and Irreversible Systems under the Influence of Light.* (*Second Communication.*)

By MEYER WILDERMAN, *Ph.D.*, *B.Sc.* (*Oxon*).

Communicated by Dr. LUDWIG MOND, *F.R.S.*

Received June 27, 1905,—Read January 25, 1906.

[PLATES 1–8.]

INTRODUCTION.

IN this communication we devote all our attention to constant reversible galvanic cells created by light. Having first shown in § 1 that the E.M.F.'s created by light in the combinations of BECQUEREL and MINCHIN, or any others, are not surface phenomena on the plates of the electrodes, but galvanic, we shall have next to establish in § 2 that the E.M.F. created by light represents a new phenomenon, and is not an ordinary thermo E.M.F. Having further shown in § 3 that all wave-lengths act as actinic rays, we shall then proceed, after the account given of the method employed to secure accurate results, to a very detailed study of constant cells reversible in respect of the cation (§ 6) and reversible in respect of the anion (§ 7) carried out with the total light of acetylene or arc, or with the total light passing coloured screens. A study (in § 5) of the chemical statics and dynamics in constant reversible cells created by light, which at the same time enables us to fix any chemical combination of cell into its proper class, must evidently proceed to the research given in § 6 and § 7. In § 8 we shall collect from the results given in § 6 and § 7 the experimental evidence in support of the physico-mathematical theory of galvanic cells given by the author in 'Roy. Soc. Proc.,' November, 1904, vol. 74. Finally, in § 9, a short outline will be given of the general laws obtained for chemical statics and dynamics under the action of light, of which galvanic cells form only a part.

§ 1. *The Experiments of* Becquerel *and* Minchin. *The Phenomena Observed by* Becquerel *and* Minchin *are not Surface Phenomena, but their Combinations form Inconstant Galvanic Cells under the Action of Light. Polarisation.*

Becquerel was the first to show that when two metallic plates are immersed in a liquid, and one is exposed to light while the other is kept in the dark, an E.M.F. is created.

Which now is the nature of this E.M.F.? Becquerel's and Minchin's (more especially the latter's) experiments brought to our knowledge peculiar facts, which all seemed to indicate that the above phenomena are surface phenomena, and strongly to oppose the author's conception of such systems as galvanic cells. What were now these observations of Becquerel and Minchin? According to Becquerel: "by depositing on one of the Ag plates a thin layer of iodide, obtained by the action of the vapour of iodine at the ordinary temperature and then exposing this plate to light, it was found that it took positive electricity from the liquid. With a thick layer of iodine on the surface of the Ag, there is on the contrary a current the inverse of the proceeding, *i.e.*, the plate exposed to light took negative electricity"; further, "whilst with precipitated chloride and bromide of silver placed on plates of platinum there is always produced a current of the same sense, the exposed plate being positive; with a layer deposited on Ag there is an effect depending upon the thickness of this layer." "These two inverse facts indicate that there should necessarily be a thickness of layer for which the electric effect is almost nothing" ('La Lumière,' vol. II., p. 129). Minchin again observes ('Phil. Mag.,' 1891, XXXI., p. 207) with AgCl, AgBr in collodion an E.M.F. in the opposite direction to that of AgI in gelatine (p. 200).

The observations of Minchin with metallic plates seem to be still more inexplicable. He tells us of "a very curious case on inversion of the current produced by light observed with silver plates immersed in water containing eosine in solution (p. 211), or in alcohol containing naphthalene red (p. 212); the E.M.F. is sometime in one, at others in the opposite direction." He made the same observation with "bismuth in water" (p. 213). In "nearly every cell used with tin plates the exposed plate was positive to the unexposed; but after a time, varying from a few minutes to a few hours, it was found that this positive current died out and was replaced by an apparently stronger current, in which the exposed plate was negative, &c." The results were similar with the "sensitive" cells which he obtained by exposing a compound of tin deposited on tin plates (obtained by acting on tin plates (alloys) with nitric acid and nitrate of ammonia and afterwards heating them till a white precipitate—the greater part evidently SnO_2—was formed on them) to light, while another tin plate without deposit is kept in the dark, both plates being immersed in methyl alcohol. He draws the conclusion that "if the deposit is not uniform, some parts of the plate give on exposure to light positive, others negative E.M.F.'s," and "such has actually been found to be the case in many experiments" (p. 222); on the whole, just as many mysterious results were obtained as there were experiments made.

The E.M.F.'s obtained changed also in their value. The "tin plates, *e.g.*, placed in alcohol, gave large deflections, but almost none, if any, chloride was introduced into the alcohol, &c.," though this ought to increase the conductivity (p. 216), &c.

Now what is more characteristic of a galvanic combination than the direction of the current in it? No galvanic combination we know of gives a current sometimes in one direction and at others in the opposite, the anode and cathode exchanging their *rôles*. At the hands of two such excellent investigators as BECQUEREL and MINCHIN only one conclusion would seem possible, a conclusion which MINCHIN, and apparently also BECQUEREL, draw all along, that the action of light upon AgCl, AgBr, AgI, and especially metal plates, leads to some special kind of surface phenomena, depending in some unknown way upon the thickness of the layer or films, and which for still unknown reasons are of a varied and complicated character.

From the first it was clear to the author that, to make substantial progress, the research must be carried out on quite different lines. It is not sufficient to notice the direction of the current; the total curve in all its complexity from beginning to end, including the deduction and induction periods, must be studied and photographed so as to get a complete, objective, and not only a partial, knowledge of the total phenomenon. The investigation must be carried out with much greater detail than hitherto, and be of quantitative, not of qualitative character, and the results so obtained be studied in connection with the chemical composition of the whole heterogeneous system and with those reactions which must take place in it under the action of light. These problems, which BECQUEREL and MINCHIN did not attempt to study, confining all their attention to the plates only, alone can lead to a satisfactory knowledge of this region.

After a long and detailed study of the method adopted, necessarily spent in obviating thermo-effects in the metallic circuit and in the cells and other sources of error, the phenomena under consideration were isolated, all complications caused by the variation of the intensity and composition of the light and other interfering phenomena being removed from the curves. The numerous varieties of curves were thus finally reduced to two special kinds only. It was only from this point that serious attention could be given to the meaning of the special course of the curves, and real advance made.

The curves of a great many of the systems studied (Ag plates, Sn plates, Pt plates, Au plates in NaCl solution) had a peculiar course. On exposing to light, a deflection, say to the right, is first obtained (the E.M.F. is positive), which gradually decreases till it becomes stationary in light, the E.M.F. still remaining positive; or it continues to decrease until it becomes "zero" and then becomes negative, and this deflection in the opposite direction goes on for some time till it becomes stationary in light. On removal of the light from the system a similar though not identical curve is obtained, which is the reversal of the first. It should be added that it has been established beyond doubt, in four different ways, that the peculiar form of the curves was not due to the inertia of the moving galvanometer mirror, but represented the true nature of the phenomena.

When we look away from the line which gives in the above-mentioned kind of curve zero deflection in the dark, we are struck by the fact that all these curves seem to have one characteristic course, as if under the action of light two opposite E.M.F.'s of two different values and with two different rates of increase were simultaneously produced, each of them ultimately reaching a maximum value, and on removal of the light the two E.M.F.'s disappear with different speeds. According as one or the other is more rapidly produced, the total E.M.F. starts by moving in one or other direction; as long as one E.M.F. preponderates over the other, the total E.M.F. continues in the same direction; when the preponderating E.M.F. reaches, or almost reaches, its maximum, while the opposite, owing to its being produced with a smaller

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ERRATUM.

Page 339, line 25: *for* "indicating a decomposition of 1 gramme electrochemical equivalent in 30,000 years," *read* "indicating the separation, by decomposition, of 1 gramme of Hydrogen or of its electrochemical equivalent in 3,000,000 years."

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only be so far a difference between the ordinary galvanic cell and our light cell, as in our case both the E.M.F. of the cell and the E.M.F. of polarisation are gradually and simultaneously produced by exposure to light, or disappear when light is removed, so that we cannot have as in ordinary galvanic cells one E.M.F. without the other.

The first important result obtained from the above explanation of the peculiar course of the curves was thus the discovery of *galvanic polarisation sui generis* created by the action of light. In the course of the induction and deduction periods we have at the same time the most efficient and reliable method of distinguishing between constant cells showing no polarisation and combinations showing polarisation. If a system shows no polarisation, and the above conception of the curve be true, there ought to be, during the induction period, only a gradual increase of the E.M.F. till the maximum is reached, and no drop, and similarly only a gradual diminution of the E.M.F. should be observed when light is removed and the system returns to its state in the dark. This is now the second kind of curves we actually obtain with a series of other systems giving constant reversible cells. A careful consideration of the reactions going on in these systems, under the action of light, shows also why they must be reversible constants.

As a result of this varied and very complicated research, which took over three years, we find that under the action of light we have a region of galvanic cells which is just as wide, just as varied, though often inaccessible to measurement, but regulated by just as solid principles, as ordinary galvanic cells. As in the case of ordinary galvanic cells, we have, under the action of light, reversible and irreversible cells, constant and inconstant cells; constant cells, the electrodes of which are "reversible in respect of the anion," constant cells, the electrodes of which are "reversible in respect of the cation"; we have cells showing polarisation owing to the gases separating on the electrodes, and cells showing polarisation owing to the electrodes changing the nature of their surfaces, &c. The chemical reactions (and chemical equilibrium) occurring in these systems and their individual nature are now perfectly clear to us and can be measured quantitatively, though the amounts of the transformations, as will be seen later on, are so exceedingly small that there is not the remotest possibility of even detecting the products of reaction by any chemical means, 10^{-9} ampère indicating a decomposition of 1 gramme electrochemical equivalent in 30,000 years.

The true meaning of the observations of BECQUEREL and MINCHIN is now apparent. "The very curious inversion of the current" observed by MINCHIN with "Ag plates immersed in water containing eosine in solution" (p. 211), "Ag plates immersed into alcohol containing naphthalene red" (p. 212), with "bismuth in water" (p. 213), with "tin plates in alcohol" (p. 216), with his "sensitive" cell, consisting of a tin plate acted upon by nitric acid, and a tin plate in methyl alcohol (p. 222), is evidently in each case due to the fact that all these systems, as now clearly appears from their composition, must form inconstant cells exhibiting polarisation.

The reason why BECQUEREL with Ag, BrAg and IAg plates found a current sometimes in one direction, sometimes in another, is not "the thickness of the layer," but the kind of combination of the heterogeneous system, of which the given plate forms only a part. An Ag-AgCl plate in NaCl solution gives a constant cell, reversible in respect of the anion; its current must, as will be shown later on, flow from the plate in the dark to the plate in the light. If, however, the layer of AgCl is very thin, such a system will soon transform under the action of light into the system (Ag in light, NaCl solution, Ag-AgCl in dark) which is inconstant, showing polarisation; Ag-AgCl plates in water form inconstant cells which exhibit polarisation and will give a current in one direction or the other. An Ag-AgCl plate placed in water containing SO_4H_2 is, in the first instance, an inconstant cell, showing polarisation; subsequently Ag_2SO_4 is formed in solution by the acid acting upon the silver plates, the system transforming into Ag plates in an Ag_2SO_4 solution, which is a constant cell reversible in respect of the cation, and its current must flow, as will be seen later on, from the plate in light to the plate in the dark. This, however, will not be the last possible transformation of such a system (Ag-AgCl in SO_4H_2 solution). Since Ag_2SO_4 is not easily soluble in water, and under the action of light the current will pass first from the plate in light to the plate in the dark, SO_4 ions will separate on the Ag-AgCl plate in light, forming Ag_2SO_4 on the same; the system (Ag-Ag_2SO_4 in light, Ag_2SO_4 solution, Ag-AgCl in the dark) will thus gradually be formed, which is reversible in respect of the anion in which the current must flow from the plate in the dark to the plate in the light. This now is exactly the combination BECQUEREL used for his actinometer, employing AgCl, AgBr, and AgI, deposited upon Ag plates immersed in a solution of "2 grammes of sulphuric acid monohydrate in 100 grammes of water," by no means a weak acid.

Again, in his experiments with AgCl, AgBr, AgI precipitated on platinum or gold plates, he puts them into pure water. Such systems must form inconstant cells, showing polarisation.

§ 2. *What is the Nature of the E.M.F. Created by Light?*

Before entering upon a study of the effect of light upon different combinations, the very first question to be clearly settled was: Are the phenomena produced by light new phenomena, or are they ordinary heat phenomena (since one plate is heated by light, the other not)?

A calculation on the basis of the quantitative measurements made for the purpose showed that if light should heat up the electrodes of different systems to the same degree as it heats up the Rubens thermopile, the total deflections which ought to be obtained under the action of light with different systems ought to be even greater than those actually observed, and the conclusion would become inevitable that the E.M.F. created by light may be nothing else but a thermo E.M.F. We take the two principal systems: Ag plates in $AgNO_3$ solution (June 6, 1903) and Ag-BrAg plates in NaBr solution (July 29, 1903).

The first system gave, with the arc at a distance = 27 centims., 5·5 centims. deflection; at the same distance the Rubens thermopile gave 101·6 centims. deflection = 1°·466 C. The thermo E.M.F. of the system in the dark being 0·0011 volt per 1° C., we ought to have got 16·35 centims. deflection, if the system were also heated by the light 1°·466 C. Similarly with the second system: the deflection observed with acetylene light at a distance = 116 centims. was 8·16 centims.; the same light heated Rubens thermopile at 116 centims. distance 0°·1208 C. The thermo E.M.F.

of the system in the dark being 0·00079 volt per 1° C., we ought to have got 8·56 centims. deflection, if the system were also heated by light 0°·1208 C.

Now the same light passing a liquid column of a bath has evidently a very much smaller heating effect than when it passes air only; the rise of the temperature of the same thermopile would have been very much smaller if it could be immersed into water instead of being in the air; it would have been smaller if, instead of very thin plates, thicker plates were used as in our experiments, &c. The first problem of all thus became to determine in each case quantitatively and by correct methods whether the observed E.M.F.'s were not entirely a thermo E.M.F.; or, if not, which part in the total phenomena was due to one effect and which part to the other.

We shall now illustrate the method used for this investigation: Let the system of two silver plates in a 0·1 normal $AgNO_3$ solution be investigated. First, the thermo E.M.F. of this combination (Ag wires in 0·1 normal $AgNO_3$) was determined (as will be described in a future publication in a section dealing with thermo-galvanic cells) and found to be, per 1° C., about 0·00011 volt. Next the rise of temperature in the quartz vessel for the same system (Ag_{pl} 0·1 normal $AgNO_3$ solution) under the action of light, under the given experimental conditions, was determined. For this a thermopile with four junctions of very thin iron-nickel wires was made and covered with shellac; 1° C. difference of temperature was found to give 65·2 millims. deflection on Nalder N1. The same thermopile was then placed in the quartz vessel containing the same two silver plates immersed in a 0·1 normal $AgNO_3$ solution (which at one time were connected with 850 ohms to a circuit, and the other time left in open circuit); two junctions of the thermopile were placed in front of the plate exposed to light, the other two near the plate kept in the dark. The deflection of Nalder N1, connected with the thermopile, on the same scale (when the arc of intensity 12·7 centims. was removed 27 centims. from quartz vessel), was in open and closed circuit between 2 and 3 millims. The heating effect upon the exposed plate under these conditions of experiments was therefore between 0°·03 and 0°·045 C., and the thermo E.M.F. for Ag in $AgNO_3$ solution, under the action of the light, thus was between $4·8 \times 10^{-6}$ and $3·2 \times 10^{-6}$ volt.

The total deflection produced by the arc upon the silver plates, immersed in the 0·1 normal $AgNO_3$ solution was next measured under the same experimental conditions (distance of the arc from quartz vessel, 26 centims., the same intensity of light, sensitiveness of Nalder N1, &c.) (see Table I., June 6, 1903). The total deflection obtained was 55 millims. Since the resistance of the solution in the quartz vessel was 13·4 ohms, of the galvanometer 834·4 ohms, the deflection caused by the thermo E.M.F. of $3·2 \times 10^{-6}$ volt was 3·2 millims., *i.e.*, about 5·8 per cent. of the total deflection observed (the total E.M.F. at 37 centims. distance from arc, this being 55×10^{-6} volt).

We thus got direct proof that under the action of light upon metallic plates two E.M.F.'s are produced: one is due to the heating of one of the plates by light and is a *thermo E.M.F.*, the chemical potential of one of the two plates becoming, owing to its rise of temperature, greater; the other is *an E.M.F. due to light at a constant temperature*, the chemical potential of the exposed plate becoming greater under the action of light.

Similar results are obtained with the constant arc, and the still more constant acetylene light, for systems (Ag-BrAg, NaBr solution, Ag-BrAg), (Ag-ClAg, NaCl solution, Ag-ClAg), (Ag-IAg, KI solution, AgI-Ag), &c.

In the experiments carried out with the system Ag-BrAg plates in a 0·1 normal NaBr solution, *e.g.*, on July 29, 1903 (*a*), acetylene light was used at a distance of 116 centims. from the quartz vessel. We get: total E.M.F. observed = 81·6 millims. or 77×10^{-6} volt; the thermo E.M.F. = $0·8 \times 10^{-6}$ to $1·2 \times 10^{-6}$ volt; the thermo E.M.F. = 1·0 per cent. to 1·5 per cent. of the total E.M.F.

§ 3. *The Rays of all Wave-lengths act both "Chemically" and as "Heat Rays," only in different Degrees.*

The next question was: Is the E.M.F. produced by the red part of the spectrum solely due to its heating action, or does it act "chemically" in the same manner as blue, violet, &c., rays—the so-called "actinic rays" of light? For this the same combinations (Ag, $AgNO_3$ solution, Ag, Ag-BrAg, NaBr solution, Ag-BrAg, &c.) were exposed to light passing different coloured screens, and the total E.M.F. so obtained compared with the thermo E.M.F. corresponding to the heating effect of the coloured light. For the first system the arc, and for the second, as before, the arc and the acetylene lights were used.

The relative values of the thermo E.M.F.'s of the total light and of the total light, passing the different screens was first determined from the heating effect of the same. A specially made thermopile with 40 iron-nickel junctions (made dead black) was introduced into the air space of the quartz vessel, placed in the bath 8 centims. behind the quartz window (as in all our subsequent experiments with the different galvanic cells) and connected with the dead-beat galvanometer (Nalder N1), used for photographing all the curves in this investigation.

The deflections of the galvanometer for the total light without screens and the total light passing a series of screens (without dye, red, green, yellow and blue) prepared for me from thin gelatine by Mr. HILGER, and placed before the quartz window of the bath, were photographed. The thickness of each screen was also measured so as to be able to introduce the correction for the absorption by gelatine; the photographed deflections so obtained gave the following results:—

With the same source of light (arc, $v = 6·6$, $A = 60$, distance from quartz vessel = 36 centims.) we got: total light, without screen, gave 89·5 centims. deflection; the same light passing the gelatine screen (0·125 millim. thick), 62·9 centims.; the red gelatine screen (0·08 millim. thick), 65·5 centims.; the yellow-green gelatine screen (0·11 millim. thick), 41·0 centims.; the blue gelatine screen (0·10 millim. thick), 49·0 centims. deflection.

A spectroscopic investigation of the light passing through the different screens showed that only the red light was perfectly pure, while the light passing through the blue and green-yellow screens contained very much red, the thickness of the gelatine having been far insufficient for its total absorption. This explains the above data with the thermopile. A pure red light, comparable with the total whole light was, however, all that was required for the present purpose.

Table A, p. 344, gives the E.M F.'s obtained in the course of this research for different combinations with the total light and with the same light passing first through the red screen in each system expressed in the same units (millims.) taken from the photographed curves, one of the plates having been exposed to light, the other kept in the dark (under identical experimental conditions).

The table shows that while the heating effect of the light passing the red screen upon the thermopile (Column VI.) is still 73·2 per cent. of the heating effect of the total light, the deflections caused in the different systems by the total light passing the red screen are only a fraction, mostly a small fraction (Columns IV. and V.) of the deflections caused by the total light without screen (Column III.).

Thus the total deflection caused by the total light could not be due to the heating effect of light alone. In Column VII., the exact values of the thermo E.M.F.'s caused by the total light are given, as they follow from direct measurements of the rise of temperature at the illuminated front plate, and of the thermo E.M.F.'s per 1° C. of the given system. Column VIII. gives the same values for the total light passing first the red gelatine screen. The difference between Columns III. (100 per cent.) and VII. gives the deflections caused by the total light at a constant temperature in per cent. of the total deflection observed in Column III. This difference shows that almost the total deflection is under our conditions of experiment created by light at a constant temperature, and only a small part principally in systems (1), (3), and (5) is due to a thermo E.M.F. created by light. Column X. gives the difference between Columns V. and VIII., *i.e.*, the deflection at a constant temperature caused by the total light passing the red gelatine screen. This Column X. shows that in both cases of the systems (2) and in (3) the light passing the red screen gives pretty considerable deflections at a constant temperature, *i.e.*, the red light is also "actinic." In case of the other systems, *e.g.* (5) or (7), the total deflection caused by red light is very small, and it is difficult to show experimentally how much of this value is a thermo E.M.F., and how much an E.M.F. at a constant temperature.

Table B, p. 345, gives the relative deflections observed for each of the systems given in the previous table with the total light, and the same light passing through the red, yellow, green and blue screens; the same values at a constant temperature are given in the last three columns.

TABLE A.

The system consists of—	Date of table.	Deflection caused by total light. A.	Deflection caused by total passing the red screen. B.	B in per cent. of A. B′.	B in per cent. of A when measured with Rubens thermopile.	The thermo E.M.F. of the total light at the distance D in per cent. of A′. $\frac{d\pi}{d\tau}$.	The thermo E.M.F. of the total light passing the red screen of the distance D_1 in per cent. of A. $\frac{d\pi'}{d\tau}$.	Deflection of the total light at a constant temperature in per cent. of A′.	Deflection of the total light passing the red screen at a constant temperature in per cent. of A′.	Distance of the light from quartz vessel. D.	Kind of cell.	Kind of light.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.	XIII.
		millims.	millims.							centims.		
(1) Ag-ClAg plates in NaCl solution	June 30, 1903	54·5 (55·5)	3·5	6·4	$\frac{65\cdot5}{89\cdot5} = 73\cdot2$	6·2–9·3	4·6–6·9	93·1–95·4	about 0–1·8	37	constant	arc
(2) Ag-BrAg plates in NaBr solution	July 29, 1903	70·2 (40 ohms shunt)	5·0	7·1	73·2	0·74–1·1	0·54–0·8	98·9–99·3	6·3–6·6	118	constant	arc
		80·0	28·5	35·6	73·2	1·0–1·5	0·7–1·1	98·5–99·0	34·5–34·9	116	constant	acetylene
(3) Ag-BrAg plate in light, NaBr solution, Ag in dark	July 20, 1903	86·5	11·9	13·76	73·2	4·7–7·1	3·4–5·2	92·9–95·3	8·56–10·4	50	constant	arc
(4) Ag plate in light, NaBr solution, Ag-BrAg in dark	July 18, 1903	75·0	2·0	2·7	73·2	—	—	—	—	67	inconstant	arc
(5) Ag plates in $AgNO_3$ solution	June 11, 1903	32·0	circa 2·0	6·2	73·2	6–9	4·4–6·6	91–94	circa 0	36(7)	constant	arc
(6) Ag plates in $AgSO_4$ solution	June 25, 1903	62·0	2·0	3·2	73·2	—	—	—	—	26	compound constant	arc
(7) Ag-IAg plates in KI solution	Feb. 17, 1904	217·0 (40 ohms shunt)	perhaps 0·5	3·2	73·2	—	—	—	circa 0	92	constant	arc

TABLE B.

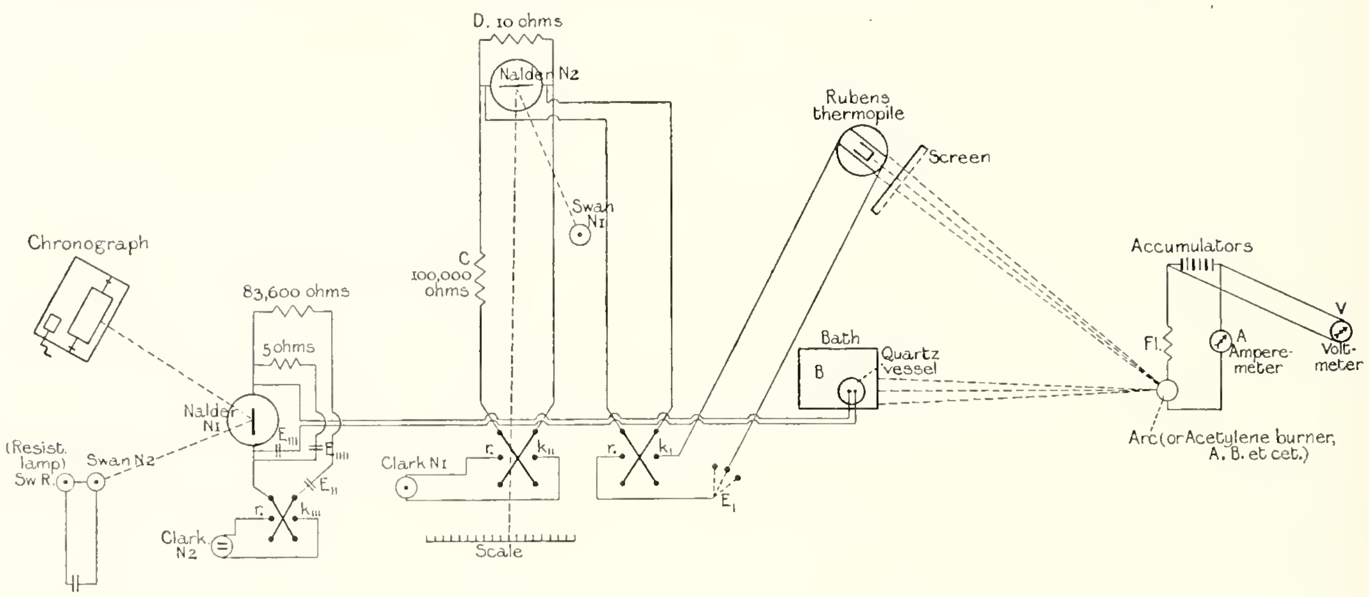
The system consists of—	Date of plate or table.	Deflection of total light. A.	Deflection of total light passing the red screen. B.	Deflection of total light passing the yellow-green screen. C.	Deflection of total light passing the blue screen. D.	B in per cent. of A = B′, red screen.	C in per cent. of A = C′, yellow-green screen.	D in per cent. of A = D′, blue screen.	B′ at a constant temperature in per cent. of A, red screen.	C′ at a constant temperature in per cent. of A, yellow-green screen.	D′ at a constant temperature in per cent. of A, blue screen.
(1) Ag-ClAg plates in NaCl solution	June 30, 1903	millims. 54·5 corr. 55·5	millims. 3·5	millims. 5·5	millims. 13·0	6·4	10·1	23·8	0–1·8	3·4–5·6	16·9–19·2
(2) Ag-BrAg plates in NaBr solution	July 29, 1903	70·2* (40 ohms shunt)	5·0*	3·5*	23·0*	7·1	5·0	32·8	6·3–6·6	4·25–4·5	32·0–32·3
		168†	60·0	41·0	48·5	35·6	24·4	28·9	34·5–34·9	23·4–23·7	27·9–28·2
(3) Ag-BrAg plate in light, NaBr solution; Ag plate in dark	July 20, 1903	86·5	11·9	6·3	10·6	13·76	7·3	12·3	8·5–10·4	2·5–4·1	7·3–9·0
(4) Ag plate in light, NaBr solution; Ag-BrAg plate in dark	July 18, 1903	75·0	2·0	1·75	29·0	2·7	2·3	38·7	—	—	$>38·7-2·7$ $= >36·0$
(5) Ag plates in $AgNO_3$ solution	June 11, 1903	32·0	circa 2·0	2·0–2·5	15·0	6·2	6·2–7·8	46·9	circa 0	circa 1·7–2·2	40·6–42·7
(6) Ag plates in $AgSO_4$ solution	June 25, 1903	62·0	2·0	—	15·5	3·2	—	25·0	—	—	$>25·0-3·2$ $= >21·8$
(7) Ag-IAg plates in KI solution	Feb. 17, 1904	217	<1·0	circa 1·0	78	<0·5	circa 0·5	36·0	circa 0	—	$>36·0-0·5$ $= >35·5$

* Arc; shunt of Nalder N1 = 40 ohms; observed.

† Acetylene; calculated for 80 centims. distance.

§ 4. *The Method of Investigation. General Arrangements of the Experiments.*

The general arrangements of the experiments are given in the following diagram:—



On the right are the arrangements for a constant source of light: acetylene or the arc was used. AB is the acetylene burner. Acetylene from the generator passes through a balance governor, regulating tap, water manometer, drying apparatus to the specially constructed burner, as described in my previous publications.

The arrangement of the arc light is as follows:—The current from the accumulators (Acc) passes through a resistance Fl (Fleming) of 3 ohms, the arc (Ar), and the ampèremeter (A); the voltmeter (V) is connected either with the terminals of the Dubosc arc, or, since the resistance is kept constant, at the terminals of the accumulators where the voltage was much higher (67 volts instead of 42), to get more sensitive reading.

The light passes to a Rubens thermopile (RTh). The wooden screen (Scr) is placed between the Rubens thermopile and the source of light. The leads from the Rubens thermopile pass to the interrupter ($E_{/}$) and reversing key ($rk_{/}$), thence to a Nalder galvanometer N2. The incandescent Swan lamp (SwN1) throws a spot of light upon Nalder N2, which falls upon a transparent celluloid scale (Sc). When the screen is closed, the spot of light gives zero deflection and the reversing key gives the E.M.F. of the thermopile in the dark, if any; when the screen is opened, the deflection of the galvanometer read on the scale gives the intensity of light.

This deflection was then calibrated in standard units. The Clark N1 is connected with the reversing key ($rk_{//}$), then with a standard 100,000 ohms manganin resistance (C), and the Nalder N2 is provided with a shunt D (10 ohms). The arrangements of the photometer are described in the former paper. The light also falls on the quartz window of the bath (B) (only one of the six quartz windows is open) and passes to the quartz vessel (QV) placed behind it at a distance of about 10 centims. The source of light is during the experiments placed at a suitable or desirable distance from it. A description of the bath has also been given. A few alterations have been made in it. The quartz vessel was placed in an ebonite holder and kept in the position by the iron stand placed on the bath. The leads from the plates in the quartz vessel were passing in the air behind thick asbestos screens fixed to the bath, and were connected with two thick flexible copper leads, one being red, the other blue, to know the direction of the current. The copper leads were connected with the Nalder galvanometer N1.

On the left of the diagram are the arrangements for photographing the deflections of the Nalder N1, caused by exposing one of the plates in the quartz vessel to light, as well as for calibrating these deflections in standard units, and for measuring the resistance of the liquid between the two plates in the quartz vessel.

The incandescent Swan lamp (SwN2) was connected with another incandescent lamp enclosed in a box and serving as an additional resistance (SwR). The spot of light, made more brilliant by the use of an increased voltage, was thrown upon the galvanometer mirror (Nalder N1) and reflected as a vertical line upon the horizontal slit of the chronograph (Ch) containing a revolving drum on which extra-sensitive bromide paper was fixed. The deflection due to the E.M.F. produced under the action of light upon the plates was photographed.

The results obtained were calibrated in standard units A Clark N2 was connected with the key ($E_{//}$), reversing key ($rk_{///}$), the manganin resistances (83,600 ohms), and the galvanometer Nalder N1 (resistance 834·4 ohms) with a shunt (5 ohms). The deflection of the galvanometer was also measured on a wooden millimetre scale placed on the drum during the time of this measurement (the measurement of the E.M.F. in the dark).

After the effect of light upon the plates was photographed and standardised, the resistance of the liquid between the plates in the quartz vessel, including the thick copper leads up to the terminals of the galvanometer, was measured by the method of KOHLRAUSCH. Arrangements were made ($E_{///}$, $E_{////}$) not to disturb during this measurement the connection at the terminals of the galvanometer. The blue lead could be disconnected from a small part of it connected with the galvanometer, and the red lead was connected at the terminal of the galvanometer with another lead of a negligible resistance which could be connected to one end of the bridge. The arrangements for these measurements can be clearly seen in the diagram.

The Constant Source of Light (Acetylene and Arc). The Measurement and Adjustment of its Intensity.

Acetylene.—In his paper "On Chemical Statics and Dynamics under the Action of Light," 'Phil. Trans.,' A, 1902, vol. 199, pp. 351–363, the author gave a detailed account of how to arrange a constant acetylene light of 250 candles and more, and how to measure the intensity of light (by means of thermopile, galvanometer, &c., &c.) with an accuracy of 0·1 per cent. (see photographic curves, plate N1; lines C_1–C_1,

C_2–C_2, giving the maximum deflection in light, are perfectly straight and parallel to a_1–b_1, a_2–b_2, which give zero deflection in the dark).

The Arc.—We had to investigate some reactions in which more actinic light than acetylene was urgently required and the use of the arc became there unavoidable. Of several arcs tried, that of KÖRTING and MATHIESEN seemed to be the best, but even it gave 15 to 20 per cent. variation, as may be seen from its photographed curves of the same plate N1.

The arc which I found most useful, and with which I succeeded in getting better results, is a Dubosc lent me by the Royal Institution. It has the disadvantage of requiring to be wound up every 5 or 10 minutes, in order that the same part of the spring may be used, but it served well our special purpose, where short exposures were required. It allows a very sensitive continuous adjustment for very small variations in the distance between the carbons. The variations on the ampèremeter show then continuous rapid oscillations of the ampères, within the narrow limits of 1 millim. or more, exceptionally 2 millims., when the total value equals 31 millims. (6·2 ampères); while the volts almost remain stationary, their variations amount to about $\frac{1}{4}$ a division out of the total of 65 to 67. Those continuous oscillations of the ampères about one mean value counteract one another, so that the integral intensity of light remains the same within very narrow limits, and this is just what we require, because a constant light is in reality only a light whose oscillations about the mean value are rapid and very small; the great regularity of the numerous curves given in this communication and the straight lines obtained for the maximum E.M.F. in light give solid evidence that I succeeded in getting a constant light with the Dubosc.

The conditions found necessary to obtain the above result are:—(1) The voltage at the terminals of the arc should be 42, at the terminals of the accumulators 65 to 67. The ampères in the circuit should be between 6·0 and 6·2. The Fleming resistances (3 ohms) inserted into the circuit should never be changed. Unless the voltage and ampères at the given resistance of circuit were exactly those given here, constant results could not be obtained with the arc. (2) The carbons were never allowed to burn down more than 1 to 2 centims., the incandescent surfaces must be kept as uniform as possible, and must be trimmed from time to time with a file. (3) There is a special distance between the carbons (between 3 and 4 millims.) which gives the best result with the arc. It is difficult to give the exact distance, which has to be determined experimentally, using a Rubens thermopile and following the indications of the ampèremeter. It is got by changing the resistance (Fl) till the desired effect is got, when the resistance (Fl) is always kept constant. (4) There is a special distance of the armature from the electromagnet, and a special tension of the spring of the arc, at which alone it gives the best result. (5) Great care must be taken in the choice of the carbons. This is a difficult point. The hard, short "Imperial Crown carbons" of the London Electric Company proved the best and most steady of all, but the author had also good results with a somewhat softer kind. The "Imperial

Crown carbons" used were 8 millims. thick on the top, 14 millims. thick below. The carbons should not be placed one at the side of the other to throw more light in the horizontal direction, as this leads to a rapid deformation of the incandescent surface of the lower carbon, but should be placed one over the other, so that the crater should come into the centre of the carbon, with only a small inclination to the side which we wish to illuminate; less light for the purpose, but more constant and for longer periods, is thus obtained, and trimming is required only at longer intervals. New carbons should never be used at once for the experiments, but only after some time, when the Rubens thermopile indicates that their intensity has come already to rest, *i.e.*, that the carbons have reached their permanent shape.

Direct measurements with the Rubens thermopile show that the intensity of the light sent by the arc horizontally in different directions differs as far as 30 to 50 per cent. according to the position of the crater with respect to the thermopile (and therefore also the quartz vessel). Similar measurements show that a variation of the voltage may lead to an essential increase of the space between the carbons, considerably change the brilliancy and intensity of the crater, and not change, or only very immaterially change, the ampères in the circuit. It is for this reason evident that at all times the intensity of the arc light cannot be indicated by the ampèremeter, but must be directly measured with the Rubens thermopile (or bolometer), care being taken that exactly the same most advantageous side of the arc which was turned to the quartz vessel should be also turned to the thermopile. For the reasons given above it is possible to get constant light for shorter periods, but it is very difficult to get every time anew the same constant intensity, as the variation in the shape and quality of carbons and the movement of the crater alone are more than enough to frustrate all attempts to get a constant light with the arc for longer periods.

The Quartz Vessel.—In this the plates and solutions of the different combinations were exposed to light. The front and back plates (45 millims. by 45 millims. and removed 13 to 15 millims. from one another), which were exposed to light, were made of quartz, all other parts were of glass, cut to the correct shape and ground at their edges. The quartz plates were cut perpendicularly to the optical axis and were optically pure. The different parts of the vessel were stuck together by means of Crookes cement and the seams covered with asphaltum. An ebonite piece fitted well into the upper part of the quartz vessel, and had two holes drilled through it to allow two copper or glass rods, to which the plates were fixed, to pass through them. The copper or glass tubes were held on the top by means of screws or shellac. In the wider part of the ebonite piece below two thin parallel slots were cut to receive the plates and keep them always in position; the front plate was about 1 millim. apart from the front quartz window.

The Plates.—They were all taken 30 millims. wide, 42 millims. long; at the top the plates had strips about 3 to 4 centims. long, both, plates and their strips, having been cut out of one and the same metal sheet. To the lower end of the thin strips of the plates wires drawn of the same piece of metal from which the plates were made, about ½ meter long, were fused to serve as leads. I am indebted to Messrs. MATTHEY and JOHNSON for having kindly prepared the plates for me, and for having supplied me with the purest metals it is possible to procure. This is necessary to avoid local action between the different metals of the same plates in a solution. The Ag was 1000/1000, the platinum was of the purest kind, as used for platinum thermometers, &c. Special care was taken to avoid thermoelectric currents in the metallic part of the circuit. The copper rods or glass tubes to which the plates were fixed serve only as supports of the plates, while the current from the plate passes along the thin insulated wires drawn of the same piece of metal as the plates, which, coming from the ebonite piece, pass in the air behind the asbestos screens of the bath. Thus the first contact of two metals in the circuit was removed half a meter from the heated plate. These junctions of the two leads in contact with copper were wrapped up in ribbons of indiarubber, both then put together and wrapped up with thick ribbons of asbestos cloth (subsequently the wires and junctions covered with several towels). The terminals of the galvanometer were also wrapped up in indiarubber, and then in very thick ribbons of asbestos, and a thick asbestos screen was besides placed in front of it, so as to ensure that the incandescent lamp used for photographing the results should have no effect upon the thermo-couple here.

Still more interfering in the present research is the thermo E.M.F. created by one of the two metal plates in contact with the liquid being heated by light, while the other is remaining in the dark, as shown in § 2. This effect can, in the nature of the case, never be completely avoided, but it may be very much reduced by the use of a bath and stirrer. The quartz vessel was placed into the large bath containing about 70 litres of water described in my previous communication, its front side being 8 to 10 centims. away from the quartz window of the bath, so that the light had first to pass through a sufficient layer of water.

Even under these conditions it was found that the rise of temperature was still for the arc about 0°·03 to 0°·045 C., when the arc was removed about 27 centims. from the quartz vessel. This, as shown before, is in our investigation enough to change the obtained results in some cases very essentially. That the effect must be much greater when the vessel containing the plates is simply held in the air is self-evident.

The Preparation of the Plates for the Experiments.

As already mentioned, the currents obtained with the metal plates were exceedingly small, the deflections on Nalder N1 ranging from several millimetres to several centimeters. Now 0·000001 of an ampère gives, with my galvanometer Nalder N1, about 85 centims. deflection; these 85-centim. deflections are therefore got with about 0·001 of a volt, the resistance of my galvanometer being 837·4 ohms, *i.e.*, 1 centim. deflection of my galvanometer is caused by about 0·000012 of a volt. Now, although the plates were prepared of one piece, underwent absolutely the same treatment, and were polished with the greatest possible care, it is found that their E.M.F. in the dark on immersing them in a liquid is, in comparison with the above values, enormous. Moreover, the E.M.F. of the plates is unceasingly varying, the mirror of the galvanometer is continuously in movement. It is only on account of the observations of Becquerel that the E.M.F. of AgCl, AgBr, AgI plates in the dark, in a closed circuit, gradually diminishes and becomes stationary, that research in this region becomes at all possible. But it is only with exceedingly well polished plates that the constant very small values of the E.M.F. finally obtained in the dark can be of real use. This is one of the very first conditions for getting good, reliable results in this region of research.

After the plates were polished, they were annealed by heating them gradually to about 120° to 140° C., and gradually cooling for several hours, repeating the operation. The plates were then polished again, to remove the thin film of oxide, and uniformly covered on one side with shellac and over this with paraffin, or with paraffin only, so that the current should pass between the two surfaces of the two plates only. The plates so prepared are then placed in the liquid of the quartz vessel for the investigation, the circuit is left closed until the E.M.F. in the dark not only ceases to vary, but gradually diminishes till it reaches the smallest possible value (in case of many plates it can be brought to about 1 centim. or less on my galvanometer, *i.e.*, to 0·00001 volt and less), which remained quite stationary for longer periods, so as no more to interfere with the research. This takes hours, sometimes 24 hours, 48 hours, sometimes much longer. Once the plates have been further finally polished by the current (this is what actually happens here) they give no more trouble. They require very little time for reaching their zero deflection on exposure to and on removal of the light, or on opening and closing of the circuit.

Photographing the Effect of Light upon the Plates.

The reactions which take place under the action of light are of so great speed, and the curves themselves are of such a complicated course, that there can be no correct and complete study of the phenomena, unless they are put on record by photography.

The nature of the phenomena with the plates is such that it became necessary to take more than one curve on the same sheet. Special arrangements were made so as to know with absolute certainty the meaning of each of the curves from their position on the plate obtained, and not to mix them up with one another, and also not to fog the very sensitive bromide paper while there was light in the room and the different measurements made. When inconstant cells, showing polarisation, will be dealt with, proof will be given in several ways that the special course of the parts of curves giving the induction and deduction periods is not due to the inertia of the moving galvanometer mirror, but represents a true phenomenon. The curves (Plates 1–8) give the originals reduced to half their size. All the details which were written down on each plate at the time of the experiment can only now be read with the help of a lens. All the data given on the plates are contained in the accounts of the experiments.

§ 5. *On the Nature of the Chemical Processes in Galvanic Cells created by Light. Light, Heat, and Pressure—Galvanic Cells.*

Becquerel and others assume that "a current is created, because a chemical reaction of decomposition goes on on the plate exposed to light," but he at once falls into difficulties when he has to explain the nature of the action of light upon metallic plates, where no "chemical reaction" can be assumed. Under the action of light in a galvanic combination a reaction takes place, *not on the exposed plate only, but on the plate in the dark as well*, that is, a reaction takes place between both plates, and the kind of reaction depends upon the composition of the system. A reaction in open circuit is not necessarily the same in closed circuit.

The general cause and condition for the creation of a galvanic cell is, that the chemical potential of the two electrodes should be different. *Since under the action of light, temperature, or pressure, the chemical potential of a substance becomes different, we must therefore get galvanic cells created by light, thermogalvanic cells, galvanic cells created by pressure,* when two plates are exposed to light of different intensity, or different temperatures or pressures. Direct observations of the direction of the current, as far as they go to the present, show that under the action of light, and with the rise of temperature, the chemical potential changes in the same manner. By this *an important analogy between the action of light and heat* is established.

Since the point of equilibrium of a system depends upon the values of the chemical potentials of its components, it is evident that a variation in the potentials under the action of light makes the system strive towards a new point of equilibrium, *i.e.*, a reaction takes place in it tending to bring it to this point. *As to the direction in which the equilibrium will be shifted by light,* this is given by my generalisation: "Each kind of equilibrium between two states of matter is, at a constant volume, on exposure to light, shifted in the direction accompanied by greater absorption of light," a principle analogous to that put up by van 't Hoff for heat (see 'Zeitschr. für Physik. Chemie,' 1902, p. 332).

Velocity of Reaction and Equilibrium.

Let us take the system: M in light, solution MA (a salt of metal M, where A is the acid radical), M in the dark, *e.g.*, Ag plate in light, $AgNO_3$ in light and in the dark, Ag plate in the dark. Here the two electrodes consist of the same metal, one is exposed to light, the other is in the dark. Both are immersed in a solution of a salt of the metal forming the electrodes. This system is reversible in light in respect of the cation and is constant.

The chemical system taken in all details consists of:—

$$\begin{array}{lcr} \overset{-}{\mathrm{Ag}}\ \text{electrode in light} & & \overset{+}{\mathrm{Ag}}\ \text{electrode in dark} \\ | & & | \\ \overset{+}{\mathrm{Ag}}\ \text{ions sat. sol.} + \overset{-}{\mathrm{NO}}_3, \overset{+}{\mathrm{Ag}}\ \text{sol. in light} & \ldots + \overset{-}{\mathrm{NO}}_3, \overset{+}{\mathrm{Ag}}\ \text{sol. in dark} & + \overset{+}{\mathrm{Ag}}\ \text{ions sat. sol. in dark.} \end{array}$$

When the current passes in the normal direction the reaction in such a system evidently consists of the following:—

$$\begin{tikzcd}
\overset{-}{\text{Ag}}\text{ electrode in light} \arrow[d] & & \overset{+}{\text{Ag}}_1\text{ electrode in dark} \\
\overset{+}{\text{Ag}}\text{ ions sat. sol. in light} + \overset{-}{\text{NO}}_{31}, \overset{+}{\text{Ag}}_1\text{ sol. in dark} \arrow[r, "", "="'] & \overset{+}{\text{Ag}}, \overset{-}{\text{NO}}_{31}\text{ sol. in dark} + \overset{+}{\text{Ag}}_1\text{ ions sat. sol. in dark,} \arrow[ur]
\end{tikzcd}$$

i.e., under the action of light there is a movement of the Ag ions from the plate in light to the plate in the dark. This disturbs the equilibrium, and a reaction takes place under the action of light, consisting of: (1) the transformation of 1 gram-atom of Ag in light into $\overset{+}{\text{Ag}}$ ions of the higher chemical potential in light; (2) the separation of 1 gram-atom of $\overset{+}{\text{Ag}}_1$ ions of the lower chemical potential in the dark upon the Ag_1 plate in the dark; (3) the transformation in the dark of 1 gram-atom of $\overset{+}{\text{Ag}}$ ions of higher potential into 1 gram-atom of $\overset{+}{\text{Ag}}_1$ ions of lower potential passing a *deduction* period. The first two reactions take place between the different parts of the heterogeneous systems, *i.e.*, between the electrodes and their ions in solution, as in all galvanic cells. The last takes place in the homogeneous liquid part.

If now we *send a current* through the system *in the direction opposite* to that of the current produced by light, while one of the plates is exposed to light and the other is kept in the dark as before, the same reaction in the opposite direction takes place. If the opposite E.M.F. is equal to the E.M.F. produced by light, no current will pass through the system; if it is greater we shall be able to reverse the reaction which previously went on in the light.

The system is therefore a *reversible* one in respect of the *cation*.

Similar is the case with the system M (metal) covered with the solid salt MA in light, M′A solution (salt of the same anion as MA) in light and in the dark, M covered with the solid MA in the dark, *e.g.*, Ag-AgCl in light, NaCl solution in light, NaCl solution in the dark, Ag-ClAg in the dark, &c., &c. These are reversible in light in respect of the *anion* and are constant.

The chemical system taken in all detail consists of—

$$\begin{tikzcd}
\underbrace{\text{Ag-ClAg electrode in light}} \arrow[d, no head] & & \underbrace{\text{Ag-ClAg electrode in light}} \arrow[dd, dotted, no head] \\
\underbrace{(\overset{+}{\text{Ag}}\text{ ions sat. sol.} + \overset{+}{\text{Ag}}, \overset{-}{\text{Cl}}\text{ sat. sol.})\text{ in light}} + \overset{+}{\text{Na}}, \overset{-}{\text{Cl}}\text{ solution in light} \arrow[d, dotted, no head] & & \\
\overset{+}{\text{Na}}, \overset{-}{\text{Cl}}\text{ sol. in dark} + & & \overbrace{(\overset{+}{\text{Ag}}, \overset{-}{\text{Cl}}\text{ sat. sol.} + \overset{+}{\text{Ag}}\text{ ions sat. sol.})}\text{ in dark.}
\end{tikzcd}$$

Such a system is reversible in light.

When the current is passing in the normal direction:—

(1) 1 gram-atom of Cl passes from the Ag-ClAg plate in light into the solution in light as $\overset{-}{\text{Cl}}$ ions of the higher chemical potential.

(2) The gram-atom of $\bar{\text{Cl}}$ ions passes from the solution in light to the solution in the dark, falling from the higher chemical potential to the lower, through a deduction period.

(3) The gram-atom of $\bar{\text{Cl}}_{,}$ ions of the lower chemical potential separates from the solution in the dark upon the Ag-ClAg plate in the dark.

And, conversely, *if the current is sent in the opposite direction*, the opposite reaction takes place, the system returning to its initial state. The mechanism of the reaction is here similar to that observed for the first system, with the only difference that the anions play here the same part as the cation in the first.

We have next to see whether such reversible heterogeneous systems are also constant cells. In a paper "On Chemical Statics and Dynamics of Galvanic Cells," which will soon be sent for publication, the author puts forward *the following generalisation* as a condition for a galvanic cell to be "truly reversible and constant": "That a galvanic cell should be reversibly constant, the chemical composition of the heterogeneous system constituting the same must, while the current is passing through it, remain constant; for this all substances in solution taking part in the chemical reaction under the action of the current (whether passing in the normal direction or in the opposite) and those which result from this reaction must not be allowed either to increase or decrease while the current is passing." This, it is shown, "can be achieved in ordinary galvanic cells if the substances taking part in and resulting from the reaction are all taken in a saturated solution in contact with their solids so as to keep the concentrations of the substances in solution each at the constant point of saturation, preventing thus the formation under the action of the current of an over-saturated or unsaturated solution of any of them. The nature and composition of an heterogeneous system being independent of the amount of the solid present in the same, all we require is evidently to keep the composition of the solution constant." The same principle, which is more of an axiomatic nature, must evidently be applied here: "That a galvanic cell should under the action of light be reversibly constant, the composition of the heterogeneous system, while the current is passing through it or is sent in the opposite direction, must remain constant."

In the first combination, the Ag plate in light and the Ag_1 plate in dark remain under the action of the current the same, whether more or less Ag ions pass from a plate into the solution or separate on it from the solution. When one gram-atom of Ag passes from one electrode into the solution, a gram-atom of Ag separates on the other electrode. Thus the total amount of nitrate of silver in solution, whether saturated or not, also remains the same. A little reflection shows also that the above system must soon reach in light a state when the ratio of Ag_1 ions to Ag and of NO_{31} to NO_3 ions will remain constant. The composition of the homogeneous liquid part, and with it of the whole of the heterogeneous systems, will thus remain under the action of the current constant. Similar is evidently the case with the *second* type of cell, reversible in respect of the anion.

The cells produced by the action of light differ from ordinary constant reversible cells as follows:—

(1) The cell is a galvanic combination only so long as it is exposed to light, so long as the chemical potentials at the two electrodes are kept different by light, while an ordinary galvanic cell is a permanent galvanic combination depending upon the permanent differences of the chemical potential at the two electrodes.

(2) We have here periods of induction before the constant maximum E.M.F. is reached, and also a period of deduction, on removal of light.

(3) The reactions under the action of the current are always accompanied by the phenomena of induction and deduction also when the maximum E.M.F. is reached.

(4) The "sensitiveness" of the electrodes to light does not always remain the same (see § 7).

(5) The E.M.F. of such a combination, and the value of the solution tension and of the chemical potential, are functions of the intensity, composition of light, of the amount of light absorbed under different physical conditions by the electrode, &c.

It remains now to consider whether there is a connection between the constancy of the above reversible systems in light and GIBBS' *rule of phases.* If we take the system reversible in respect of the anion, p. 353,

$$N = \text{Ag, Cl, Na, H}_2\text{O} = 4,\ m = \text{Ag, ClAg, and solution} = 3,$$

if AgCl and solution in light and in the dark are regarded each as one phase, but $m = 5$ if AgCl and the solution in light and in the dark are regarded as in two different phases. In this case $m = n+1$, the system is one of complete equilibrium, and such combinations ought to be constant.

Similar is the case with the cells reversible in respect of the cation (p. 352) $n = (\text{Ag}, \text{NO}_3, \text{H}_2\text{O}) = 3$, while $m = 2$ if the same substance in light and in the dark is regarded as one phase; but $m = 4 = n+1$ if it is regarded as two phases.

Before passing to the account of the experiments made, I should like to state that all curves obtained during the first year and a-half were rejected, and that when it was thought that all possible errors in the methods, &c., were removed to justify complete confidence in the results obtained, all previous experiments were repeated again. Some of the more important results were investigated, after this a second time, after an interval of a year or more, for greater security.

§ 6. *Experimental Results obtained with Constant Cells reversible in respect of the Cation.*

(*a*) *The system* Ag *plate in light,* AgNO_3 *solution in light,* AgNO_3 *solution in the the dark,* Ag *plate in dark.*—Plates of the 3rd and 4th, 5th, 6th, 8th, 11th, (18th), 19th (*a*), 19th (*b*), 19th (*c*) of June, 1903, under N1, 2, 3, 4, 5, 6, 7, 8, 9, and Table I., pp. 390–391, give the investigation of the different problems, connected with constant cells, reversible in respect of the cation, carried out on the system Ag in light, $AgNO_3$ solution, Ag in the dark. Each of the plates contains a series of curves. All of them have exactly the same course, showing that the curves are characteristic of this type of cell. The part of the curves *a–b*, representing a straight line, gives the position of the spot of light from the galvanometer Nalder N1, when both Ag plates are in the dark in a closed circuit (the E.M.F. in the dark having reached in the different plates constant and very small values); the part of curve *b–c* is of a logarithmic shape and gives the gradually increasing deflection of the galvanometer, when one of the Ag plates is exposed to light (at *b*); the part of the curve *c–d* is again a straight line, and gives the maximum deflection of the galvanometer ultimately reached in light; the straight line *c–d* is running parallel to line *a–b*, indicating that the system (Ag plate in light, $AgNO_3$ solution in light, $AgNO_3$ solution in the dark, Ag plate in the dark) acquires after a time (after the period given by *b–c*) a constant new state in light, given by *c–d* as characteristic of it, as is its constant state in the dark, given by *a–b*; the further part of the curve *d–e* gives the gradual diminution of the deflection of the galvanometer, when light is removed from the system (at *d*), *i.e.*, the gradual drop of the E.M.F. of the system, when the system gradually passes in the dark from its constant state in light to its constant state in the dark. When this return is complete, we must evidently get again a straight line, a continuation of *a–b*; before then it only gradually approximates to its constant state in the dark.

We note that the system passes in light from the state *a–b* to the state *c–d* only gradually (not suddenly) and so also on removal of the light the system passes in the dark from the state *c–d* to the state *a–b* only gradually (not suddenly). It follows from this that *b–c* and *d–e* represent truly gradual transformations in the state of the system, passing from one constant state in the dark to another constant state in light and *vice versâ*. We shall call *b–c* the *induction* period, *d–e* the *deduction* period, since the phenomena here are similar to the phenomena of "induction" and "deduction," observed for chemical reactions (such as CO and Cl_2) in light and dealt with in the author's papers on "Chemical Statics and Dynamics in Light," 'Phil. Trans. Royal Society,' 1903, 'Zeit. Physik. Chemie,' June, December, 1902, &c., &c.

We notice the course of the induction and deduction periods; *b–c*, as well as *d–e*, change their curvature, have a point of inflection, changing sign from positive to negative or *vice versâ*, and the curves approximate asymptotically either to *c–d* or *a–b*. Their equations, meaning and content are given in the "Preliminary Communication of Galvanic Cells produced by Light," 'Roy. Soc. Proc.,' Nov., 1904, and will be specially dealt with later on.

Plate of June 3 *and* 4, 1903 (16 *Curves*), *N*2, *Table I.*

The Ag plates, prepared as described in § 4, and polished before by the current, were immersed in a 0·25 normal $AgNO_3$ solution. To know the direction of the current in the solution, the red and blue thick leads from the quartz vessel were always connected in the same way to the galvanometer (Nalder N1), the red lead with the plate exposed to light. On replacing the light cell by a Daniell, it was found that the plate in light behaves to the plate in the dark as Zn to Cu in the Daniell, *i.e.*, under the action of light the current passes in the solution from the Ag plate in light to the Ag plate in the dark.

After an hour the E.M.F. in the dark was = 2·7 centims. to the right, and next day (June 4) = 1·5 centims. to the right = $17·6 \times 10^{-9}$ ampère = $15·0 \times 10^{-6}$ volt. The arc (Dubosc) was at 65 volts, 6 ampères. The intensity of light (measured by the Rubens thermopile on Nalder N2) = 11·6 centims. (right and left), while the calibration with the Clark and 100,000 ohms resistance and 10 ohms shunt of galvanometer gave a deflection (right and left) 19·8 centims. The quartz vessel was removed from the quartz window 8 centims. There are 16 curves on this plate, numbered in the order they were taken. After the curves were taken, the sensitiveness of the galvanometer (Nalder N1) was measured in standard units (Clark, 83,600 ohms in circuit; 5 ohms in shunt of galvanometer); the same was (right and left) = 17·4 centims. The resistance of the solution in the quartz vessel between the plates 13·4 ohms.

Curve N1 shows that, after the first exposure to light, the system passes on removal to the light, in the dark, through a deduction period, back to its former state in the dark before illumination, approaching it however very slowly and asymptotically.

Curves N2, 3, 4, 5, 6 (distance of the arc from the quartz vessel 37 centims.) show that after the first exposure we get the same curves on repetition of the experiment, at the same distance of the arc from the quartz vessel. The return to the state in the dark on removal of the light is complete in (2), (3), (4), (5), (6), after curve (1), when the small residue of energy created by the heating effect of light, which leaves the system only very slowly, is allowed to remain in it (2 millims. deflection). The deflections are in (1) 20 millims., in (2) 19 millims. (corr. 21 millims.), in (3) 17 millims. (corr. 19 millims.), in (4) 18 millims. (corr. 20 millims.), in (5) 18 millims. (corr. 20 millims.), in (6) 16 millims. (corr. 18 millims.), *i.e.*, if not corrected, 20, 19, 17, 18, 18, 16, average = 18 millims. = $21·1 \times 10^{-9}$ ampère = $18·0 \times 10^{-6}$ volt; if corrected, 20, 21, 19, 20, 20, 18 millims. = average 19·7 millims. = $23·1 \times 10^{-9}$ ampère = $19·6 \times 10^{-6}$ volt.

This shows beyond dispute that the system is in the dark in one constant state, and in light (of a given intensity) again in another.

The curves N7, 8, 9, 10, 11, 12 test the same point at a distance of 33 centims. After N7, 8, the curves were taken uninterruptedly one after another to see whether the system quickly returns to the same two states in light and in the dark. We find that on every occasion the curves reached, or almost reached, in the dark the same line *a*–*b*, and again every time it returned in light to the same line *c*–*d*. The author did not always wait for complete return of the system to the last millimetre, because he had to keep the light of the arc constant during the whole series of experiments.

The deflection in (7) is 24 millims. (removed from zero deflection in the dark 2 millims.); in (8) 24 millims. (corr. 26 millims.); in (9) 26 millims. (corr. not returned 2 millims.); in (10) 24 millims. (corr. 26 millims., not returned 1 millim.); in (11) 23 millims. (corr. + 2 millims. + 1 millim. = 26 millims.); in (12) 23·5 millims. (corr. + 2 millims. + 1 millim. = 26·5 millims.). Thus we have for N7, 8, 9, 10, 11, 12, if not corrected, deflections: 24, 24, 26, 24, 23, 23·5, average 24 millims. $= 28{\cdot}1 \times 10^{-9}$ ampère $= 24 \times 10^{-6}$ volt; and if corrected: 24, 26, 26, 26, 26, 26·5 $= 25{\cdot}8$ millims. $= 30{\cdot}2 \times 10^{-9}$ ampère $= 25{\cdot}7 \times 10^{-6}$ volt (at a distance of 33 centims. of the arc from quartz vessel). We find $37^2 \times 18 = \mathbf{24{\cdot}6 \times 10^3}$ (not corr.) and $33^2 \times 24 = \mathbf{26{\cdot}1 \times 10^3}$ (not corr.) and $37^2 \times 19{\cdot}7 = \mathbf{27 \times 10^3}$ (corr.) and $33^2 \times 25{\cdot}3 = \mathbf{27{\cdot}5 \times 10^3}$ (corr.), *i.e., the deflection in light, or the E.M.F. created by the light, is directly proportional to the intensity of the light.*

Curve (13) *consists of* 5 *Curves.*—Here the author purposely arranged that the system, after it reached its constant state in light, should in each successive experiment be more and more removed from its state in the dark, passing smaller and smaller parts of the deduction period by every time screening the system from light for shorter and shorter periods. We see that however much or little the system traversed the part of the curve giving the deduction period, it always returns in light to the same line, and this is very clear evidence that the state of the system in light of a given intensity and composition is a strongly defined and a constant one. In the last portion of N13 the system was allowed to completely return to its initial state in the dark, and this shows again that the point in the dark is a perfectly defined and a constant one.

Curves 14, 15, 16 were again taken one after another. We get again three deflections of the same magnitude, 21 millims., 21 millims., 21 millims. (corr. 24 millims., 24 millims., 24 millims. $= 28{\cdot}1 \times 10^{-9}$ ampère $= 24{\cdot}0 \times 10^{-6}$ volt).

The investigation of the above system was then extended for longer periods to observe the influence of time upon the E.M.F. produced.

Plate of June 5, 1903 (9 *Curves*) *N*3, *Table I.*

The same system from June 3 was left short-circuited in the dark. The deflection in the dark was $= 15 \times 10^{-6}$ volt. Experimental data, see Plate N3, Table I.

The deflections obtained at 26 centims. distance are: in (1) 36 millims. in (2) 35 millims. (corr. 37 millims.), in (3) 34 millims. (corr. 37 millims.), in (4) 33 millims. (corr. 36 millims.) = average 34·5 millims. $= 40{\cdot}55 \times 10^{-9}$ ampère $= 34{\cdot}4 \times 10^{-6}$ volt if not corrected, and = average 36·5 millims. $= 42{\cdot}8 \times 10^{-9}$ ampère $= 36{\cdot}4 \times 10^{-6}$ volt if corrected. (Intensity of the arc 12·5 right and left.) The deflections obtained at 36 (7) centims. distance are: in (5) 17 millims., in (6) 15·7 millims., in (7) 17 millims., in (8) 19 millims., in (9) 17 millims., average = 17 millims. = 19×10^{-9} ampère = $16{\cdot}9 \times 10^{-6}$ volt (at intensity of the arc = 11·5 centims.); for light intensity = 12·1 centims., the average deflection = 17·9 millims. The law of intensity:

$$36^2 \times 17{\cdot}9 = \mathbf{23{\cdot}2} \times 10^3 \quad \text{and} \quad 26^2 \times 34{\cdot}5 = \mathbf{23{\cdot}3} \times 10^3 \text{ if not corrected,}$$
$$37^2 \times 17{\cdot}9 = \mathbf{24{\cdot}5} \times 10^3 \quad \text{and} \quad 26^2 \times 36{\cdot}5 = \mathbf{24{\cdot}7} \times 10^3 \text{ if corrected.}$$

Plate N4 of June 6, 1903 (4 *Curves*), *New Carbons* ("*Imperial Crown*"), *Table I.*

The same combination from June 3 was taken. Experimental data, Plate N4, Table I. The deflection obtained at a distance of 26 centims. is: in (1) 55 millims., in (2) 54 millims. = average 54·5 millims. = $63{\cdot}9 \times 10^{-9}$ ampère = $54{\cdot}4 \times 10^{-6}$ volt.

The deflection obtained at a distance of 36 centims. is: in (3) 28 millims., in (4) 28 millims., average = 28 millims. = $32{\cdot}8 \times 10^{-9}$ ampère = $27{\cdot}9 \times 10^{-6}$ volt. We get for the law of intensity: $36^2 \times 28 = \mathbf{36{\cdot}3} \times 10^3$ and $26^2 \times 54{\cdot}5 = \mathbf{36{\cdot}8} \times 10^3$.

Plate of June 8, 1903 (4 *Curves*) (3*rd Curve interrupted, Plate N*5), *Table I.*

The same system from June 3, the same carbons as on June 6; the E.M.F. in the dark = 93×10^{-6} volt. Deflections obtained at 36 centims. distance were: in (1) 29 millims., in (2) 29 millims., in (3) interrupted, in (4) 26 to 27 millims. = average 28·2 millims. = 33×10^{-9} ampère = $28{\cdot}1 \times 10^{-6}$ volt.

Comparing the tables of the 4th and 5th of June with that of the 6th of June, and 8th, 11th, 18th, and 19th of June, which will subsequently be dealt with:—

	Date June, 1903.	Distance of arc from quartz vessel.	Distance of quartz vessel from quartz window.	Deflection of Nalder N1.	Intensity of light in deflections of Nalder N2 = A.	Calibration of Nalder N2, B.	Calibration of Nalder N1.	Intensity of light A/B.	Deflection of Nalder N1 for the intensity of light 0·586 = A/B.
		centims.	centims.	millims.					millims.
	4	37	8	18 19·7 (corr.)	11·6	19·8	17·4	0·586	**18** **19·7** (corr.)
	5	36 (7)	8	17	11·5	19·8	17·4	0·581	**17**
New carbons, "Imperial Crown"	6	36	8·5	28	12·7	19·8	17·4	0·641	**25·6**
	8	36	8·5	28·2	13·5	19·8	17·4	0·682	**24·2**
	11	36 (7)	8·5	32	12·9	19·8	17·4	0·651	**25·2**

This table shows that the different composition of the carbons alone can considerably vary the intensity of their light and influence the value of the E.M.F. produced.

On the 4th and 5th of June we got practically the same deflection (18 and 17 millims.). On the 6th and 8th of June we got with the new carbons 28 millims., and the same result was obtained with the same carbons several days later, on the 11th of June. When corrected for the same intensity of light, A/B = 0·586, we still get for the 6th, 8th, 11th of June the values 25·6, 24·1, 25·2 millims. instead of 18, 17 millims. of the 4th and 5th of June. Thus the composition of light, not only the intensity of the light, changes with different carbons used. It makes also a further investigation necessary, whether a small oxidation of the Ag plates, or change in their brightness which may take place in time, may also influence the values of the E.M.F.'s obtained.

Plate of June 11, 1903 (6 *Curves*), *N*6, *Plate I.*

The same system from June 3. The circuit was always kept closed between the experiments of the different days, and the same plate was always exposed to light. The E.M.F. in the dark = 2·7 centims. = $26·9 \times 10^{-6}$ volt. Experimental data, Plate N6, Table I., pp. 390–391. Distance of the arc from quartz vessel 36 (37) centims. The carbons the same as on the 6th and 8th of June.

Curve N1 obtained with the total white light gave = 32 millims. deflection = $37·5 \times 10^{-9}$ ampère = $31·9 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection at a constant temperature = 32 millims. − (1·9 to 3 millims.) = 29 to 30·1 millims. Curve N2 was obtained with the blue gelatine screen; the deflection in light = 15 millims. = $17·6 \times 10^{-9}$ ampère = $14·5 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 15 millims. − (1·3 to 2 millims.) = 13 to 13·7 millims. Curves N3 and N3_1, obtained with the green-yellow gelatine screen, gave 2·5 millims. and 2·5 millims. = average 2·5 millims. deflection = $2·9 \times 10^{-9}$ ampère = $2·4 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 2·5 millims. − (1·3 to 1·9 millims.), *i.e.*, no E.M.F. at a constant temperature can be shown to be produced by light. Curves N4 and N4_1, obtained with the red gelatine screen, gave 2 millims. and 1·5 millims. = average 1·75 millims. deflection = $2·1 \times 10^{-9}$ ampère = $1·8 \times 10^{-6}$ volt. Corrected for the thermo E.M.F., the deflection = 1·8 millims. − (1·4 to 2·1 millims.), *i.e.*, no E.M.F. at a constant temperature can be shown to be produced by light.

From the above it is to be seen that the E.M.F. produced by light at a constant temperature is principally due to the blue rays of the spectrum and very little to the red or yellow parts of the same. (The results obtained with the gelatine screens contain no correction for the gelatine.)

In § 2 it has been shown that the thermo E.M.F. caused by the total light forms about 6 to 9 per cent. of the total E.M.F.

An application of a correction of 9 per cent. for the heat effect of total light gives the following results for the law of light intensity *at a constant temperature*:—

June 3 and 4 . $37^2 \times 16{\cdot}4 = \mathbf{22{\cdot}5} \times 10^3$ and $33^2 \times 21{\cdot}8 = \mathbf{23{\cdot}7} \times 10^3$ (not corrected).
$37^2 \times 17{\cdot}9 = \mathbf{24{\cdot}5} \times 10^3$ and $33^2 \times 23{\cdot}0 = \mathbf{25{\cdot}0} \times 10^3$ (corrected).
June 5 . . . $36^2 \times 16{\cdot}3 = \mathbf{21{\cdot}1} \times 10^3$ and $26^2 \times 31{\cdot}4 = \mathbf{21{\cdot}2} \times 10^3$ (not corrected).
$37^2 \times 16{\cdot}3 = \mathbf{22{\cdot}3} \times 10^3$ and $26^2 \times 33{\cdot}2 = \mathbf{22{\cdot}5} \times 10^3$ (corrected).
June 6 . . . $36^2 \times 25{\cdot}5 = \mathbf{33{\cdot}0} \times 10^3$ and $26^2 \times 49{\cdot}6 = \mathbf{33{\cdot}5} \times 10^3$,

i.e., since the thermo E.M.F. is directly proportional to the intensity of light, we find, as before, that *the E.M.F. produced by light at a constant temperature is also (as the total E.M.F.) directly proportional to the intensity of light.*

Experiments of June 18, 1903 (2 *Curves*), *Table I.*

The Ag plates of June 3, 1903, were polished again and covered on one side with paraffin, and placed into a 0·0041 normal $AgNO_3$ solution. Resistance of liquid in quartz vessel = 840 ohms. After $1\frac{1}{2}$ hours the E.M.F. in the dark was still 17 centims. to the right, but further diminution became slow. At a distance of the arc of 27 centims. a deflection = 20 millims. was obtained. (Experimental data, Table I., pp. 390–391.)

A comparison of this result with those subsequently obtained on June 9 shows that the formation of an oxide layer, if any, can take place with pure silver plates only very slowly, and that it is the Ag plate which gives the E.M.F. under the action of light, not a layer of oxide.

Comparing, on the other hand, the above result with those of June 6, and calculating the deflection for the same resistance of the liquid (847·8 instead of 1674), the same intensity of the light $\left(\frac{A}{B} = 0{\cdot}641\right)$, the same distances (37 centims. instead of 27 centims.), we get 20·7 millims. deflection (with the newly polished plates) instead of 28 millims. on June 6 (with plates which were several days in solution). This seems also to indicate either that the problem of getting a light of constant composition with the arc is still awaiting its solution, or that a small diminution in the brightness of the Ag plates still takes place in time, though very slowly.

Plates (*a*), (*b*), (*c*) *of June* 19, 1903 (*Table I.*). *The Influence of the Concentration of the Solution upon the E.M.F. of the System.*

Three different concentrations of $AgNO_3$ were rapidly investigated one after another in the course of about 3 hours, between 11.30 A.M. and 2.20 P.M., passing from the dilute solution to the more concentrated one. The solutions used were 0·0041 normal (Table *a*), 0·025 normal (Plate *b*), and 0·25 normal (Table *c*). Experimental data, see Table I.

Plate (*a*) *contains* 5 *Curves.*—The same solution as used on June 18, but the E.M.F.

in the dark is $= 1{\cdot}9$ centim. to the left $= 37{\cdot}4 \times 10^{-6}$ volt (instead of to the right). The deflections obtained in N1, 2, 3, at a distance of the arc = 36 (37) centims., are after the first, 10·5 millims., 10·5 millims. = average 10·5 millims. $= 20{\cdot}6 \times 10^{-6}$ volt, and a distance of 26 (7) centims., 19 and 18 millims. = average 18·5 millims. $= 36{\cdot}3 \times 10^{-5}$ volt. We find again: $37^2 \times 10{\cdot}5 = \mathbf{14{\cdot}4} \times 10^3$ and $27^2 \times 18{\cdot}5 = \mathbf{13{\cdot}5} \times 10^3$. The resistance of the liquid is, as before, 840 ohms.

Plate (b) contains 5 *Curves.*—The Ag plates are in a 0·025 normal $AgNO_3$ solution. The curves are, for this reason, steadier and better defined. It took an hour for the galvanometer to steady quite down, the deflection in the dark becoming only 1 centim. to the left $= 10{\cdot}3 \times 10^{-6}$ volt. Experimental conditions were the same as in (*a*). Resistance of the liquid in the quartz vessel between the Ag plates was found to be 146 ohms. The deflections obtained at 27 centims. distance were: 40·5 millims. in N1, 30·5 millims. (corr. 34·5 millims.) in N2, 32·5 millims. (corr. 38 millims.) in N3, = average 37·3 millims. corr. $= 43{\cdot}6 \times 10^{-9}$ ampère $= 38{\cdot}4 \times 10^{-6}$ volt. The deflections obtained at 37 centims. distance were 23·5 millims. in N4, and 21·5 millims. (no corr. required) in N5 = average 22·5 millims. $= 26{\cdot}3 \times 10^{-9}$ ampère $= 23{\cdot}2 \times 10^{-6}$ volt. We find again: $37^2 \times 22{\cdot}5 = \mathbf{30{\cdot}8} \times 10^3$ and $27^2 \times 37{\cdot}3 = \mathbf{27{\cdot}2} \times 10^3$.

Plate (*c*) *contains* 4 *Curves.*—The Ag plates were now in a 0·25 normal $AgNO_3$ solution. The resistance of the solution between the plates in the quartz vessel was found to be 16·5 ohms. The E.M.F. in the dark = 0·9 centim. to the left $= 9{\cdot}0 \times 10^{-6}$ volt. The carbons in (*a*), (*b*), (*c*) were the same, care having been taken to stop the arc at once after the curves of each series were taken and the measurement of the deflection with the Rubens thermopile made (all other measurements were subsequently made). The deflections obtained at a distance of the arc = 27 centims. are: 40 millims. in N1, 38 millims. (corr. 40 millims.) in N2, average 40 millims. $= 46{\cdot}9 \times 10^{-9}$ ampère $= 39{\cdot}8 \times 10^{-6}$ volt. The deflections obtained at a distance 37 centims. are: 26 millims. in N3, 21 millims. in N4 (no corr. was required) = average 23·5 millims. $= 27{\cdot}6 \times 10^{-9}$ ampère $= 23{\cdot}4 \times 10^{-6}$ volt. We get again: $37^2 \times 23{\cdot}5 = \mathbf{32{\cdot}2} \times 10^3$ and $27^2 \times 40 = \mathbf{29{\cdot}2} \times 10^3$.

Let us now compare the results of Tables (*a*), (*b*), (*c*), obtained under exactly the same conditions, except the concentrations of the $AgNO_3$ solution.

The resistance of the Nalder N1 was again measured and found to be 834·4 ohms. Thus the resistance in the circuit was in (*a*) 1674·4 ohms, in (*b*) 980·4 ohms, in (*c*) 851·4 ohms. We get the following table:—

Concentration of the $AgNO_3$ solution.	Resistance in circuit in ohms. W.	Deflection obtained at the distance of light from QV = 27 centims. $D_{\prime}$.	$D_{\prime} = (a)$ ampère. A.	The E.M.F. at 27 centims. distance. W.A.	Deflection obtained at the distance of light from QV = 37 centims. $D_{\prime\prime}$.	$D_{\prime\prime} = (a')$ ampères. A′.	The E.M.F. at 37 centims. distance. W.A′.	Intensity of arc.	Calibration of Nalder N2.	Calibration of Nalder N1.
in (*a*): **0·0041** n.	1674·4	millims. 18·5 (average)	$21{\cdot}7 \times 10^{-9}$	$\mathbf{36{\cdot}3} \times 10^{-6}$ v.	millims. 10·5 (average)	$12{\cdot}3 \times 10^{-9}$	$\mathbf{20{\cdot}6} \times 10^{-6}$ v.	11·2	17·2	17·4
in (*b*): **0·025** n.	980·4	37·3 (,,)	$43{\cdot}6 \times 10^{-9}$	$\mathbf{38{\cdot}4} \times 10^{-6}$ v.	22·5 (,,)	$26{\cdot}3 \times 10^{-9}$	$\mathbf{23{\cdot}2} \times 10^{-6}$ v.	11·2	17·2	17·4
in (*c*): **0·25** n.	851·4	40·0 (,,)	$46{\cdot}9 \times 10^{-9}$	$\mathbf{39{\cdot}8} \times 10^{-6}$ v.	23·5 (,,)	$27{\cdot}6 \times 10^{-9}$	$\mathbf{23{\cdot}4} \times 10^{-6}$ v.	11·2	17·2	17·4

Thus we find *that the total E.M.F.* (*i.e.*, the E.M.F. under the action of light at a constant temperature + the E.M.F. due to the heating of the exposed plate and liquid in front of it) *of constant cells reversible in respect of the cation is independent of the concentration* of the $AgNO_3$ solution.

A correction of 9 per cent. for the heating effect gives for the law of intensity and *the volts obtained at a constant temperature* the following data in (*a*), (*b*), (*c*). For the law of intensity we get :—

In (*a*) $37^2 \times 9{\cdot}55 = 13{\cdot}1 \times 10^3$ and $27^2 \times 16{\cdot}83 = 12{\cdot}3 \times 10^3$.
In (*b*) $37^2 \times 20{\cdot}5 = 28{\cdot}1 \times 10^3$ and $27^2 \times 33{\cdot}9 = 24{\cdot}7 \times 10^3$.
In (*c*) $37^2 \times 21{\cdot}4 = 29{\cdot}3 \times 10^3$ and $27^2 \times 36{\cdot}4 = 26{\cdot}5 \times 10^3$.

For the volts obtained we get : *at 27 centims. distance* in (*a*) $33{\cdot}0 \times 10^{-6}$ volt, in (*b*) $34{\cdot}9 \times 10^{-6}$ volt, in (*c*) $36{\cdot}3 \times 10^{-6}$ volt. *At 37 centims. distance* in (*a*) $18{\cdot}7 \times 10^{-6}$ volt, in (*b*) $21{\cdot}1 \times 10^{-6}$ volt, in (*c*) $21{\cdot}3 \times 10^{-6}$ volt.

§ 7. *Experimental Results obtained with Constant Cells Reversible in Respect of the Anion.*

I. *The System* (Ag-AgCl *in Light, Decinormal* NaCl *Solution in Light, Decinormal* NaCl *Solution in the Dark*, Ag-AgCl *in the Dark*). *Plate N*10 *of June* 30 (10 *Curves were taken*), *Table II.*

The Ag plates of the previous investigation (Ag plates in $AgNO_3$ solution) were covered on one side with shellac and paraffin, and coated on the other with an extraordinarily thin layer of AgCl by immersing them in water containing a merest trace of HCl acid. A decinormal NaCl solution was brought into the quartz vessel, some AgCl was put on the bottom, then the Ag plates were fixed in the quartz vessel. Experimental data see Table II., pp. 392–393.

The curves give a deflection to the left; the course of the induction (*b*–*c*) and deduction periods (*d*–*e*–*f*) show that the system is constant, gives no polarisation. After the induction period has passed, a constant E.M.F. (*e*–*d*) is obtained (whether the whole light or coloured screens are used). On removing the light from the system it returns, passing the deduction period, to its former state in the dark, as is to be seen from the straight line *f′*–*f″* reached by the system, which is a continuation of the straight line *a*–*b* before the induction period. The current is flowing in the solution from the plate in the dark to the plate in light. The deflections obtained at a distance of the arc = 37 centims. were : in N1, 56 millims. (did not return 2 millims.) ; in N2, 53 millims. (corr. 55 millims.), average = 55·5 millims. = 59×10^{-9} ampère = $51{\cdot}8 \times 10^{-6}$ volt ; at a distance of 50 centims. : in N3, 31 millims. ; in N4, 34 millims., average = 32·5 millims. = $34{\cdot}6 \times 10^{-9}$ ampère = $30{\cdot}4 \times 10^{-6}$ volt.

The law of intensity: $37^2 \times 55{\cdot}5 = \mathbf{76} \times 10^3$ and $50^2 \times 32{\cdot}5 = \mathbf{81} \times 10^3$, *i.e.*, the E.M.F. is directly proportional to the intensity of light.

Curves N5 and N6 give the deflections obtained with the red screen, curves N7 and N8 with the blue screen, curves N9 and N10 with the yellow-green screen, all at a distance of the arc from quartz vessel = 37 centims. The ratio of the deflections in millimetres of the white light : blue : yellow-green : red = 54·5 (corr. 55·5 millims.) : 13 millims. : 5·5 millims. : 3·5 millims., or in per cent. of the total light without screen = 100 per cent. : 23·4 per cent. : 9·9 per cent. : 6·3 per cent. This shows in the first instance that the so-called "actinic" rays act most. Calculating now the thermo E.M.F. at a distance of 37 centims. we get:—

If $d\pi/d\tau$ is put, according to GOCKEL, = 0·00014 volt, then, since the rise of temperature was

$$\frac{(0^\circ{\cdot}03 \text{ to } 0^\circ{\cdot}045) \times 27^2 \times 19{\cdot}8 \times 15{\cdot}5}{37^2 \times 12{\cdot}7 \times 16{\cdot}7} = 0^\circ{\cdot}023 \text{ to } 0^\circ{\cdot}035 \text{ C.},$$

the thermo E.M.F. = (3·2 to 4·8) . 10^{-6} volt; since the sensitiveness of Nalder N1 was 94·4 centims. per 10^{-6} ampère, we get the thermo E.M.F. on Nalder N1 = 3·5 to 5·2 millims. for the total light, and = 2·5 to 3·8 millims. for the red screen, = 2·6 to 3·7 millims. for the yellow-green screen, = 2·4 to 3·6 for the blue screen. The ratio of the total light : blue : yellow-green : red, at a constant temperature is thus: (93·1 to 95·4 per cent.) : (16·9 to 19·2 per cent.) : (3·4 to 5·6 per cent.) : (0 to 1·8 per cent.). (No correction is made here for the absorption of light by the gelatine of the screens.)

(2) *On July* 1, next day, the cell was no more constant, but showed already a small *polarisation* of 3·6 millims., the above maximum deflection returning back 3·5 millims., remaining only then constant. The maximum constant deflections on the drum at a distance of 37 centims. were: (53·5), 66·1, 68·3, 70·3, 68·3 millims. = average 68·2 millims. = $72{\cdot}5 \times 10^{-9}$ ampère = $63{\cdot}6 \times 10^{-6}$ volt. On shutting the screen, the spot of light first passed the zero deflection in the dark by 3·5 millims., returning to zero deflection, where it remained constant.

It follows from the above: (1) The sensitiveness of the plates remaining in the dark 21 hours increased from about 55 millims. to about 68 millims. (2) The current passing in light from the plate in the dark to the plate in light, the AgCl of the plate in light, or the upper surface of the same, evidently transforms into Ag, while on the plate in the dark new AgCl was formed; the system thus transformed on the previous day into (Ag in light, ClNa solution, Ag-ClAg in dark). A direct investigation of a similar system (Ag in light, BrNa solution, Ag-BrAg in dark) showed that such systems form inconstant cells and show *polarisation.* An analysis of the reactions going on in such systems shows also that this must be the case. By the action of Cl_2 upon this system *the system is reversed* to the original combination, the formed Ag transforming back into AgCl, and the constant cell is again obtained.

II. *The System (*Ag-BrAg *in Light, Decinormal* NaBr *Solution in Light, Decinormal* NaBr *Solution in the Dark,* Ag-BrAg *in the Dark).*

On this system the properties of constant cells reversible in respect of the anion were studied in great detail, the deflections obtained being very large and suitable for quantitative investigation. The AgCl was removed from the Ag plates with a CNK solution, the Ag plates polished again, covered on one side with shellac and paraffin, then immersed into a solution of Br_2 in water for a short time. A very thin layer of AgBr was thus deposited on the same.

These plates were first used on July 25 and 27, 1903, for the investigation of the system (Ag-BrAg plate in light, KNO_3 solution, Ag-BrAg in the dark), which is an *inconstant* cell, and showed polarisation. The same Ag-BrAg plates, carefully washed, were now placed in the quartz vessel containing a decinormal NaBr solution and solid AgBr, and a *constant* cell was obtained. Arc and acetylene light were used; the last, however, almost exclusively on account of its very much greater constancy.

(1) *Plate* N11 *of July* 28, 1903 (3 *Curves*).—Acetylene light used. For experimental data, see Table III., pp. 392–393. Forty-five minutes after the circuit was closed the E.M.F. in the dark was still = 18 centims. to the left = 167×10^{-6} volt. Though it has not yet reached its constant minimum, 3 curves were taken in succession to see the character of the results immediately after the circuit is closed. The curves did not return to zero deflection in the dark. During the time a curve was taken, the E.M.F. in the dark shifted to a new point. The deflections obtained in N1, 2, 3 were 60 millims., 74 to 75 millims., 74 to 75 millims., the distances between *a–b* and *d–d* in N1, 2, 3 were 11 millims., 20 millims., 20 millims. Thus the results corrected for the variation of the E.M.F. in the dark are: 49 millims., 44 to 45 millims., 45 to 46 millims., = average 46·3 millims. = $49{\cdot}2 \times 10^{-9}$ ampère = $43{\cdot}2 \times 10^{-6}$ volt.

(2) *Plate* N12 *of July* 29 (*a*) *contains* 9 *Curves, Table III.*—The plates from July 28 were left short-circuited till the next day: the E.M.F. in the dark found to be = 1·5 centims. = $14{\cdot}2 \times 10^{-6}$ volt to the right (*i.e.*, in an opposite direction to that of the previous day). On opening and shutting the circuit, the spot of light always returned to the same position on the scale. The acetylene light was in all experiments at the same distance of 116 centims. from the quartz vessel; the intensity of light coming from the burner was changed by screening more and more the light with the chimney of the burner and measuring its intensity with the Rubens thermopile. The deflections obtained with N1*, 2, 3, 4, 5, with the intensity of the acetylene = 71 millims. deflection, were 84, 81, 82, 80, 81 millims., average = 81·6 millims. = $86{\cdot}7 \times 10^{-9}$ ampère = $76{\cdot}1 \times 10^{-6}$ volt. The curves return after the deduction period (if we wait sufficient time) to their former position in the dark, as is well illustrated by curves N2 and N4; in N3 and N5 we did not

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* After the maximum deflection was reached, screen of chronograph fell down, so that the deduction period was not photographed.

photograph the last 3 or 4 millims. of the ends of the deduction period so as to avoid the danger of several lines coinciding on the photographic sheet, but I waited, after the screen of the chronograph was shut, some time till it could be assumed that the deduction was complete.

The deflections obtained with N6 and 7, with the intensity of acetylene = 39 millims., were: 43·5 and 44·5 millims., average = 44 millims. = $46·8 \times 10^{-9}$ ampère = $41·0 \times 10^{-6}$ volt. The curve in N6 was allowed to return to its E.M.F. in the dark, in N7 the last few millimetres of the end of the deduction period were not photographed. The deflections obtained with N8 and 9, with the intensity of acetylene = 28·5 millims., were: 32·5 and 31 millims., average = 31·8 millims. = $33·8 \times 10^{-9}$ ampère = $29·6 \times 10^{-6}$ volt; the last 2½ to 3 millims. were not photographed, but, as before, I waited till the deduction period must have become complete.

From the data given in the above table we get again the law of intensity—81·6 : 71 = **1·15**; 44 : 39 = **1·13**; 31·8 : 28·5 = **1·12.**

The above data obtained for light of the same intensity (and composition) on repetition of the experiment: 84, 81, 82, 80, 81 millims.; 43·5 and 44·5 millims.; 32·5 and 31 millims. give a sufficient illustration that during the time the above curves were taken, and with light of such small intensity, which cannot affect essentially the composition of the electrode exposed to the same, the same deflection is obtained, and this shows that the chemical potential and solution pressure of the same plates remain constant. The cell is reversible, as it follows from the consideration of the reactions going on in it, and from the course of the above curves, the induction and deduction periods of which show no polarisation, while the system always returns to its former state, whenever on removal of the light we allow the deduction period to become complete. It is constant, as is shown by the shape of the parts of the curves giving the induction and deduction periods, from the straight line *c–c*, obtained in light, parallel to the line *a–b* in the dark, and from the fact that on repetition of the experiment the same maximum deflection is obtained.

(3) *Plate* 13 (*b*) *of July* 29, 1903, *contains* 13 *Curves, Table III.*—The same system was investigated a few hours later, first with acetylene, then with the arc.

Acetylene light and coloured screens (*curves N*1, 2, 3, 4, 5, 6, 7), *Experimental data, see Table III., pp.* 392–393.

In curve N1 the total acetylene light as before was used, at a distance = 116 centims.; the deflection was 80 millims. The next curves, M2, 3, 4, 5, were taken with the *red* screen: N2 and 3 at a distance of the acetylene light from the quartz vessel = 116 centims., N4 at a distance of 80 centims., N5 at a distance of 57 centims. The maximum constant deflections obtained for N2 and 3 were 28 and 29 millims. = average 28·5 millims. = $30·3 \times 10^{-9}$ ampère = $26·6 \times 10^{-6}$ volt in N4 = 60 millims. = $63·7 \times 10^{-9}$ ampère = $55·9 \times 10^{-6}$ volt, in N5 it was about 3 millims. greater than could be got on the photographic paper (115 millims.), since the photographed curve shows that the constant maximum was very nearly reached, *i.e.*, the deflection was 118 millims. = $125·3 \times 10^{-9}$ ampère = 110×10^{-6} volt. (In all the above curves the deduction period was allowed to become complete.)

We get the law of intensity also with red light (curves N2, 3, 4, 5, taken in about half an hour) : $116^2 \times 28·5$ = **383,600** ; $80^2 \times 60$ = **384,000** ; $57^2 \times 118$ = **383,500**.

Curves N6 and 7 were taken with the blue and yellow-green screen at a distance of the light from quartz vessel = 80 centims., and the deflections obtained were 48·5 and 41 millims.

Thus we get for the same 80 centims. distance of light from quartz vessel :—

	Total light (without screen).	Total light passing red screen.	Total light passing blue screen.	Total light passing yellow-green screen.
Deflections observed . . .	168 millims. = $156·6 \times 10^{-6}$ volt	60 millims. = $55·9 \times 10^{-6}$ volt	48·5 millims. = $45·2 \times 10^{-6}$ volt	41 millims. = $38·2 \times 10^{-6}$ volt
In per cent. of total light . .	100	35·7	28·9	24·4

We get the remarkable result that the light of acetylene passing the red screen gives with the above system the greatest deflection, and the yellow-green the smallest, as if two maxima were present, one near the red end of the spectrum, the other near the blue end of the spectrum. (This result compare with the results obtained with the arc.)

The above results change very little when corrected for the thermo E.M.F., which is = 1 to 1·5 per cent. of the total E.M.F. created by light (see § 2).

For the law at intensity at a constant temperature we get (July 29) :—

In (*a*) : 80·4 : 71 = **1·13**   43·3 : 39 = **1·11**   31·3 : 28·5 = **1·10**
80·8 : 71 = **1·14**   43·6 : 39 = **1·12**   31·5 : 28·5 = **1·11**

instead of 1·15, 1·13, 1·12.

In (*b*) : $116^2 \times 28·1$ = **378** × 10^3, $80^2 \times 59·1$ = **378** × 10^3, $57^2 \times 116·2$ = **378** × 10^3,
$116^2 \times 28·2$ = **380** × 10^3, $80^2 \times 59·4$ = **380** × 10^3, $57^2 \times 116·8$ = **380** × 10^3,

instead of 384 × 10^3 ; 384 × 10^3 ; 384 × 10^3 ; 387 × 10^3.

Arc (DUBOSCQ) *and Coloured Screens, Plate* 13 *of July* 29, 1903 (*Curves N*3, 9, 10, 11, 12, 13). *Experimental data, see Table III.*

We get for the total light without screen in N8 = 76 millims., in N10 = 69 millims., in N14 = 71·5 millims., for the blue screen in N9 = 23 millims., for the red screen in N11 = 5 millims., for the yellow-green screen in N12 = 3·5 millims. (for the thinner colourless gelatine screen, 0·12 millim. thick), in N13 = 64·5 millims. All the above curves were taken at a distance of the arc from quartz vessel = 118 centims. At the conclusion (after the photographic paper sheet was taken off) I measured also the deflection obtained on the drum with the total light of the arc at a distance of the arc from quartz vessel = 89 centims. and found it to be 120 millims. (we denote this measurement as N14). The deduction period was allowed to become complete or almost complete in most of the curves (N8, 10, 11, 12). We get for the law of intensity :

$$118^2 \times \frac{76+69+71{\cdot}5}{3} = \mathbf{100{\cdot}5} \times 10^4,\ 118^2 \times \frac{69+71{\cdot}5}{2} = \mathbf{97{\cdot}7} \times 10^4 \text{ and } 89^2 \times 120 = \mathbf{95{\cdot}0} \times 10^4.$$

Calculating the thermo E.M.F. created by light, we get : the rise of temperature of the exposed plate $= \frac{(0^\circ{\cdot}03 \text{ to } 0^\circ{\cdot}045) \times 27^2 \times 19{\cdot}8 \times 9{\cdot}2}{118^2 \times 12{\cdot}7 \times 17{\cdot}05} = 0^\circ{\cdot}013$ to $0^\circ{\cdot}009$ C., $\frac{d\pi}{d\tau} = 0{\cdot}00079$ volt, the sensitiveness of Nalder N1 = 93·9 centims. per 10^{-6} ampère, shunt of galvanometer = 40 ohms, the resistance of the solution in quartz vessel = 43 ohms, &c., therefore the thermo E.M.F. = 0·74 to 1·1 per cent. of the total deflection of the total light (without screen).

Thus we get :—

	Total light.	Red gelatine screen.	Blue screen.	Yellow-green screen.
Total E.M.F., in millims .	70·2 (corr. 72·2)	5	23	5
The thermo E.M.F., in millims.	0·54 to 0·8	0·39 to 0·57	0·3 to 0·45	0·25 to 0·4
E.M.F. at a constant temperature, in millims .	69·4 to 69·8	4·4 to 4·6	22·5 to 22·7	4·6 to 4·75
In per cent. of the total light	100	6·3 to 6·6	32·4 to 32·7	6·6 to 6·8

Here we find for the arc : (1) that the light passing the red screen gives a smaller deflection than the light passing the blue gelatine screen, while between the red and yellow-green screens no essential difference is found ; (2) that all parts of the spectrum give E.M.F.'s at a constant temperature (*i.e.*, also the red and yellow-green parts of the spectrum). Contrary to this, we found with acetylene that the red screen gave greater deflections than the yellow-green, *i.e.*, that two maxima are existing, one in the red, the other in the blue. It follows from this that the arc is richer in blue, the acetylene in red rays.

I next proceed to the account of comparative experiments, where either the concentrations of the same solutions or the temperature were changed. All these experiments had to be carried out in as short a time as possible, to avoid the effect of time after previous illumination. On the other hand, really good experiments require very small values of the E.M.F. in the dark, which is not possible without waiting with new solutions for a long time. I had therefore to choose the most suitable middle course. I waited only till the diminution of the E.M.F. in the dark became so small that it could but little affect the values of the deflections obtained. The deduction period of only one of the curves taken for every concentration was allowed to become complete, since all we required to know in these experiments was the maximum deflection only. The first deflection in each concentration is for obvious reasons the more reliable one.

III. *Plate N14 of July* 30, 31, 1903. *Influence of Concentration, Table IV.*

In all the following experiments the distance of the acetylene from the quartz vessel was 116 centims., the intensity of the acetylene was 67 millims. (right and left), while the calibration of Nalder N2 was = 170 millims. right and left.

(*a*) The system, used on July 29 and consisting of Ag-BrAg plates immersed into a decinormal NaBr solution, is again investigated. The E.M.F. in the dark = 1·3 centims. = $12{\cdot}1 \times 10^{-6}$ volt, to the left. The resistance of the solution = 43·4 ohms. N1 gave 114 millims., N2 113·5 millims. deflection, average = 113·75 millims. = 120×10^{-9} ampère = 106×10^{-6} volt. In Curve N1 the deduction period was photographed to within 3 millims. from *a–b*.

(*b*) A great part of the solution was removed and distilled water added. The resistance of the solution in the quartz vessel = 137 ohms. After an hour and an half the E.M.F. in the dark became = 6·0 centims. to the left, and was found almost constant during 15 minutes. N3 gave 114 millims., N4 116 millims. deflection = average 115 millims. = $123{\cdot}3 \times 10^{-9}$ ampère = $118{\cdot}5 \times 10^{-6}$ volt; the deduction period of N3 was photographed to within 6 millims. of its completion.

(*c*) Removed all the solution, added distilled water, so that a very dilute solution was formed. The resistance was found to be 400 ohms. After about 15 minutes the E.M.F. in the dark was still 14 centims. to the right, but seemed almost constant during about 10 minutes. Curves N5 gave 80 millims. and N6 86 millims. deflection = average 83 millims. = $91{\cdot}3 \times 10^{-9}$ ampère = $108{\cdot}8 \times 10^{-6}$ volt. Since N6 was the last curve for the day I allowed its deduction period to become complete. We thus have:—

$$
\begin{array}{llllll}
\text{In } (a) \text{ in N1}: & E = c \times w = (834{\cdot}4 + 43{\cdot}4)\ 114 & = 100{\cdot}1 & \times 10^{3} & = \mathbf{106{\cdot}3} \times 10^{-6} & \text{volt.} \\
\quad\text{in N2}: & = (834{\cdot}4 + 43{\cdot}4)\ 113{\cdot}5 & = 99{\cdot}63 & \times 10^{3} & = \mathbf{105{\cdot}8} \times 10^{-6} & \text{volt.} \\
\text{In } (b) \text{ in N3}: & = (834{\cdot}4 + 137)\ 114 & = 110{\cdot}7 & \times 10^{3} & = \mathbf{117{\cdot}5} \times 10^{-6} & \text{volt.} \\
\quad\text{in N4}: & = (834{\cdot}4 + 137)\ 116 & = 112{\cdot}7 & \times 10^{3} & = \mathbf{119{\cdot}7} \times 10^{-6} & \text{volt.} \\
\text{In } (c) \text{ in N5}: & = (834{\cdot}4 + 400)\ 80 & = 98{\cdot}75 & \times 10^{3} & = \mathbf{104{\cdot}9} \times 10^{-6} & \text{volt.} \\
\quad\text{in N6}: & = (834{\cdot}4 + 400)\ 86 & = 106{\cdot}2 & \times 10^{3} & = \mathbf{112{\cdot}8} \times 10^{-6} & \text{volt.} \\
\hline
 & \text{Average of N1, 2, 3, 4, 5, 6} & & & = \mathbf{111{\cdot}3} \times 10^{-6} & \text{volt.} \\
\hline
 & \text{Average of the more reliable obser. N1, 3, 5}: & & & \mathbf{109{\cdot}7} \times 10^{-6} & \text{volt.}
\end{array}
$$

The electric conductivities show that the concentrations used were from the decinormal to about centinormal.

Experiments of July 31 (6 *Curves taken*) :—

(*a*) A decinormal NaBr solution was used. The resistance of the solution = 50 ohms (distance between the plates a little increased), the E.M.F. in the dark = 3 millims. to the left. Two curves were taken (N7 galvanometer shaken, had to lower screen of chronograph), N8 gave 120 millims. deflection = $127{\cdot}5 \times 10^{-9}$ ampère = $112{\cdot}7 \times 10^{-6}$ volt, the deduction allowed to become complete to within 2 millims.

(*b*) The solution from quartz vessel was removed and a normal NaBr solution added. The resistance was about 5 ohms. The E.M.F. in the dark = 14 centims. to the left. N9 gave 105 millims., N10 gave 106 millims. deflection, average 105·5 millims. = 112×10^{-9} ampère = 94×10^{-6} volt.

(*c*) Removed the greater part of the solution, added water. The resistance found = 163·4 ohms. The E.M.F. in the dark = 7 centims. to the right. Curves N11 gave 92 millims., N12 gave 99 millims. deflection, average 95·5 millims. = $101{\cdot}5 \times 10^{-9}$ ampère = $101{\cdot}2 \times 10^{-6}$ volt. The concentrations of July 31 were therefore between about normal and 0·025 normal NaBr solution. We thus get :—

$$\begin{array}{lrl}
\text{In } (a') \text{ in N8}: & E = c \times w & = (834{\cdot}4 + 50)\ 120 = 106{\cdot}1 \times 10^3 = \mathbf{112{\cdot}7} \times 10^{-6} \text{ volt.} \\
\text{In } (b') \text{ in N9}: & & = (834{\cdot}4 + 5)\ 105 = 88{\cdot}14 \times 10^3 = \mathbf{93{\cdot}6} \times 10^{-6} \text{ volt.} \\
\quad\text{in N10}: & & = (834{\cdot}4 + 5)\ 106 = 88{\cdot}97 \times 10^3 = \mathbf{94{\cdot}5} \times 10^{-6} \text{ volt.} \\
\text{In } (c') \text{ in N11}: & & = (834{\cdot}4 + 163{\cdot}4)\ 92 = 91{\cdot}8 \times 10^3 = \mathbf{97{\cdot}5} \times 10^{-6} \text{ volt.} \\
\quad\text{in N12}: & & = (834{\cdot}4 + 163{\cdot}4)\ 99 = 98{\cdot}78 \times 10^3 = \mathbf{104{\cdot}9} \times 10^{-6} \text{ volt.}
\end{array}$$

$$\text{Average of N8, 9, 10, 11, 12} \qquad = \mathbf{100{\cdot}6} \times 10^{-6} \text{ volt.}$$

$$\text{Average of more reliable obser. N8, 9, 11} : \mathbf{101{\cdot}3} \times 10^{-6} \text{ volt.}$$

The above observations were extended for another day.

On August 1.—The solution of (*c*′) was left in the dark short-circuited for about 18 hours. The resistance was found to be 142·9 ohms (the two plates became a little nearer). The E.M.F. in the dark = 1·0 centim. to the left. On the drum of the chronograph a millimetre scale was placed and the deflection read. Distance, intensity of the acetylene, &c., &c., the same as on the previous day. The deflections obtained were 105 millims., 104·5 millims., 106 millims. = average 105·2 millims. = $111{\cdot}7 \times 10^{-9}$ ampère = $109{\cdot}1 \times 10^{-6}$ volt, the deduction periods having been allowed to become complete. From this it follows :—

$$\begin{array}{lrl}
\text{N13 } (c''): & E = c \times w & = (834{\cdot}4 + 142{\cdot}9)\ 105 = 102{\cdot}6 \times 10^3 = \mathbf{109} \times 10^{-6} \text{ volt.} \\
& & = (834{\cdot}4 + 142{\cdot}9)\ 104{\cdot}5 = 102{\cdot}1 \times 10^3 = \mathbf{108{\cdot}4} \times 10^{-6} \text{ volt.} \\
& & = (834{\cdot}4 + 142{\cdot}9)\ 106 = 103{\cdot}6 \times 10^3 = \mathbf{110} \times 10^{-6} \text{ volt.}
\end{array}$$

$$\text{Average} = \mathbf{109} \times 10^{-6} \text{ volt.}$$

All the above results show that *the E.M.F. of galvanic combinations reversible in respect of the anion is independent of the concentration of the solution.* No correction for the thermo E.M.F.'s was considered necessary to employ, in view of experimental errors here.

IV. *The Effect of Previous Illumination upon the Increase of Sensitiveness of the System in the Dark.*

On July 28 we exposed the Ag-BrAg plate 3 times to the light of the acetylene at the great distance of 116 centims. Remaining then about 16 hours in the dark, the sensitiveness of the plates increased from 61 to 69·2 millims., *i.e.*, by about 0·5 millim. (0·7 per cent.) per hour. It was then exposed 9 times on the 29th (Plate *a*) to very weak acetylene light at 116 centims. distance. After this it increased in about 4 hours by about 3 millims., *i.e.*, 0·7 millim. (0·9 per cent.) per hour. Then we exposed the plates 7 times on the same day (Plate *b*) to acetylene, and 8 times to the more powerful arc; during the next 16 hours in the dark the sensitiveness also increased more rapidly, namely, from 83 to 114 millims., *i.e.*, by about 1·5 per cent. per hour (July 30).

The system was then exposed to light 6 times. After the system remained further 22 hours in the dark we found on further exposure to acetylene (on July 31) only a small increase, if any; the maximum of this increase could be from about 113·8 to $\frac{123 \times 885}{878} = 124$ millims., *i.e.*, 10·2 millims. (or 0·47 per cent.) per hour (compare *a* with *a′*). The system was then exposed to acetylene 6 times, again at a distance of 116 centims., and left in the dark about 18 hours, till August 1. On exposure to light only a very small increase, if any, was found; the maximum increase was from 96 to 105, *i.e.*, 0·5 millim. (or 0·5 per cent.) per hour (compare *c′* and *c″*). If we assume that the E.M.F. is independent of the concentration, (*c″*) will mean $\frac{105 \times 977 \cdot 3}{877 \cdot 7} = 117$ millims. for the same total resistance in the circuit of 877·7 ohms, *i.e.*, there is a decrease from 124 to 117 millims., *i.e.*, a decrease of 0·4 millim., or 0·4 per cent., per hour. I conclude from this, as well as from numerous other observations to be dealt with later on, that the influence of previous illumination upon the subsequent increase of sensitiveness in the dark is the greatest at the beginning, and is gradually diminishing to small values, when the sensitiveness of the system seems to become constant. It is possible even that after this a decrease in the sensitiveness to light takes place.

The increase of sensitiveness of Ag salts, till they reach a constant maximum, when kept in the dark, after previous illumination, must not be mixed up with the ordinary effect of light upon Ag salts, in darkening them. The last naturally increases to some extent their capacity of absorption of light. The numerous photographic curves obtained on repetition of the same experiment after short time intervals prove, however, conclusively that when, as in our case, a weak source of light is judiciously employed, the variation in the AgBr salts due to this effect is so small that the same deflections are always obtained. But when after the same illumination the two measurements are separated not by short intervals only, but by many hours, a great increase of the E.M.F. obtained is first observed. Similar results were obtained with other systems, also with black Cu-CuO plates in a solution of NaOH, *i.e.*, where no darkening of the electrodes could come into consideration. On the other hand, no such increase of sensitiveness was found with the Ag-AgBr plate of the system which was kept the whole time in the dark. It follows from this that we meet here with a peculiar phenomenon which we may call "*continuous light sensibilisation in the dark.*" The light previously absorbed continues to produce some variation in the plate in the dark: it either continues first to form Ag_2Br, Cu_2O (Ag_2Br gives, according to BECQUEREL, a greater E.M.F. than AgBr), and then continues to form Ag from Ag_2O, Cu from Cu_2O (which give smaller E.M.F.'s), or it produces some other physical variations in the crystals of AgBr or CuO (it is known, *e.g.*, that the process of "ripening" of emulsions in the dark is accompanied by an increase of size of the crystals of BrAg).

We must give our attention to curves N9 and N10, obtained on July 31, with normal NaBr solution: here, on the top (at *b*), we notice for the first time the formation of a very small *polarisation*, though its presence is not yet to be seen at the end of C, when the deduction period begins. This suggests that, as in the case of Ag-ClAg in NaCl solution, under the repeated exposure to light the transformation of AgBr or Ag_2Br into Ag has gone far enough towards the formation of the system (Ag plate in light, NaBr solution, Ag-BrAg plate in the dark) which is in light an inconstant cell.

V. *Influence of Temperature upon the E.M.F. obtained in Cells Reversible in Respect of the Anion* (*Table V.*).

Some modifications had to be made in the method. It was found impossible to determine the influence of temperature upon the E.M.F. obtained with the above plates up to 40° or 50° C., as before, since the paraffin and the shellac split off from the plates. I covered for this reason the plates on all sides with a (thick) coating of AgBr.

In all the experiments the whole of the front surface of the front plate was always exposed to light, while its back and the two surfaces of the back plate remained always in the dark.

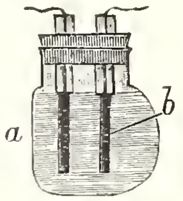

Fig. 1.

Since the quartz vessel, for which Crookes' cement has to be used, could not be well employed for higher temperatures, vessel fig. 1 was used instead. (*a*) represents a very thin and very clear round flat side, about 5 centims. diameter, flattened down with the flame in the thin bulb. The front Ag-BrAg plate was about 5 millims. from the flat side.

The use of ice or hot water and stirrer enabled us to cool or heat up the bath quickly, and the 70 litres water of the same enabled us to keep the temperature constant for longer periods. Experimental data, see Table V.

(α) *The System* Ag-BrAg *Plates in* 0·1 *normal* KBr *Solution* (*8th, 9th, and 13th July*, 1904).

July 8.—The deflections (200 ohms shunt of galvanometer) were :

In N1 = 75·4 millims., in N2 = 75·4 millims. at **38°·1** C. (at 3 P.M.).
In N3 = 81·7 millims., in N4 = 81·7 millims. at **20°·8** C. (at 5 P.M.).

July 9.—The E.M.F.'s in the dark = 6 millims. to the right (no shunt) in N1 and N2, = 5 millims. to the right (no shunt) in N3 and N4. The deflections obtained (200 ohms shunt of galvanometer) were :

In N1 = 107 millims., in N2 = 108 millims. at **2°·8** C. (at 12.30 P.M.).
In N3 = 102 millims., in N4 = 101 millims. at **27°·1** C. (at 1.30 P.M.).

July 13.—The E.M.F.'s in the dark (200 ohms shunt) = 5·5 centims. to the right in N1 and N2, = 1·7 centims. to the right in N3 and N4, = 1·5 centims. to the right in N5 and N6. The deflections obtained (200 ohms shunt of galvanometer) were :

In N1 = 133 millims., in N2 = 133 millims. at **48°·5** C.
In N3 = 136 millims., in N4 = 133 millims. at **33°·5** C. (at 12.30 P.M.).
In N5 = 140 millims., in N6 = 136 millims. at **2°·3** C. (at 3.40 P.M.).

If the results are taken for the intensity of light of the previous experiments = 48·3 to 48·5 millims., 6 per cent. must be added, and we get :

In N1 = 141 millims., in N2 = 141 millims. at **48°** C.
In N3 = 144 millims., in N4 = 141 millims. at **33°·5** C.
In N5 = 148 millims., in N6 = 144 millims. at **2°·3** C.

The results obtained with the decinormal KBr solution thus are the following :—

(1) On the 8th, 9th and 13th of July the three series of results differ from one another, the E.M.F. of the combination (with freshly covered plates) becoming again greater when it was left in the dark for longer periods after illumination.

(2) In each series the deflections obtained, differ only by a few millimetres, *i.e.*, *the variation of the E.M.F. created by light with temperature can only be small*

(β) *The System* Ag-BrAg *Plates in* 0·1 *normal* LiBr *Solution* (*July* 20, 1904).

The Ag-BrAg plates used here were those used above, but subjected between the 15th and 19th of July to the action of the solutions of HBr (to be dealt with later on). On the 20th the influence of temperature upon the same Ag-BrAg plates in a decinormal LiBr solution was investigated. Experimental data, see Table V. The E.M.F. in the dark was in N1 and N2 = 1·9 centims. to the right (200 ohms shunt), in N3, N4, N5 = 3 millims. to the left (200 ohms shunt). The deflections obtained (200 ohms shunt of galvanometer) were:

In N1 = 126 millims., in N2 = 119 + 6 = 125 millims. at **23°** C. (at 1.15 to 1.40 P.M.).
In N3 = 117·5 millims., in N4 = 108 + 17 = 125 millims., in N5 = 107 + 17 = 125 millims. at **3°** C. (at 5 P.M.).

These results show again that the variation of the E.M.F. with temperature can only be small.

(γ) *The System* Ag-BrAg *Plates in* 0·1 *normal* NaBr *Solution* (*Plate N*19), *Table V.*

Seven months later, on February 15, 1905, again an experiment was instituted with 0·1 normal NaBr solution, but for a smaller temperature interval, so that one side of each plate could again be covered with shellac and paraffin. The Ag-BrAg plates were not the same as before. The maximum deflections obtained (no shunt used with the galvanometer):

In N1: 85 millims. at **1°** C.; in N2: 87·5 millims. at **21°·5** C.

The results therefore similar to those obtained before with KBr and LiBr solutions.

VI. *On the E.M.F.'s obtained with the same* Ag-BrAg *plates in different Bromides. Influence of the Cation in Cells Reversible in respect of the Anion* (*Table VI.*).

The Ag-BrAg plates covered on all sides with BrAg are those used from July 8, 1904, till July 13 with a decinormal KBr solution, from July 15 till July 19 with solutions of HBr, and on the 20th with the LiBr solutions. In these experiments the same plate was always exposed to light, but now I turned the plates, so that the plate which previously always was in the dark was now exposed to light, while the plate which was always exposed to light was now kept in the dark.

(α) *Experiments of July* 25, 1904:—

(*a*) The decinormal **LiBr** solution from July 20 was now used. The E.M.F. in the dark = 3 millims. (200 ohms shunt) to the right. Intensity of acetylene = 46·5 millims. Calibration of Nalder N2 = 16·0 centims., of Nalder N1 = 16·0 centims. The deflections obtained (with 1000 ohms shunt of galvanometer) were: In N1 = 116 millims. (deduction not complete 2 millims.), in N2 = 117 millims. (deduction complete), average = 116·5 (at 12°·5 C. and 1.15 P.M.).

(*b*) A decinormal **KBr** solution was now used; intensity of acetylene, calibration of Nalder **N2** and N1 the same as in (*a*). The E.M.F. in the dark = 1·5 centims. to the left (1000 ohms shunt). The deflections obtained (with 1000 ohms shunt of galvanometer) were: in N3 = 120 millims., in N4 = 117, average = 118·5 millims. (at 13°·5 C. and at 3.0 P.M.).

(*c*) A decinormal **NaBr** solution was now used: intensity of acetylene = 47 millims., calibration of Nalder N2 and N1 the same as before; the E.M.F. in the dark = 4·7 centims. to the left (1000 ohms shunt of galvanometer). The deflections obtained (1000 ohms shunt of galvanometer) were: in N5 = 136 millims., in N6 = 112 millims., in N7 = 114 millims., in N8 = 114 millims. = average 119 millims (at 13°·5).

It follows from the above (1) that *the E.M.F. of a combination reversible in respect of the anion is independent of the cation of the salt in solution*; (2) comparing the results obtained with the decinormal LiBr solution on July 25 and 20, we find that the Ag-AgBr plate kept the whole time in the dark is less sensitive to light than the plate which had been previously exposed several times to light; (3) we find that the deflections of July 19 and 20 are essentially smaller than those of July 13 instead of being of the same values or even of greater. The reason of this is probably that the Ag-BrAg plates were previously acted upon from the 15th till the 19th of July by BrH *which gradually transformed the* Ag (*or* Ag_2Br) *on the surface previously formed back into* AgBr.

(β) The influence of the cation upon the E.M.F. obtained was again investigated between the 1*st and 7th of February*, 1905. Each of the plates was on one side covered again with shellac and paraffin. The plates had a thick coating of BrAg. On February 3 the sensitiveness of the plates reached already such a value that the E.M.F. seemed to change no more on further remaining in the dark, after previous illumination.

February 3, 1905, *Plate* 16 :—

0·1 norm. **KBr** sol. gave: in N1, 96·5 millims.; in N2, 96·5 millims. deflection;
0·1 norm. **NaBr** sol. gave: in N3, 85 millims.; in N4, 86 millims. deflection.

Intensity of acetylene = 20·05 right and left, Nalder N2 = 15·75 centims., Nalder N1 = 19·2 centims.

February 6, 1905, *Plate* 17 :—

0·1 norm. **NaBr** sol. gave: in N1, 84 millims.; in N2, 77 millims.; in N3, 78 millims. deflection;
0·1 norm. **LiBr** sol. gave: in N4, 91 millims.; in N5, 95 millims.; in N6, 91 millims. deflection.

Intensity of acetylene = 21·5, Nalder N2 = 16·05 centims., Nalder N1 = 19·2 centims.

February 7, 1905, *Plate* 18 :—

0·1 norm. **LiBr** sol. gave : in N1, 92 millims. deflection ;
0·1 norm. **NH_4Br** sol. gave : in N2, 98 millims. ; in N3, 98 millims. deflection.

Intensity of acetylene = 21·5, Nalder N2 = 16·05 centims., Nalder N1 = 21·2 centims. As the distance of the light from the systems was 116 centims., the thermo E.M.F.'s under my conditions of experiment could be neglected.

The results obtained with KBr, NaBr, LiBr, NH_4Br, confirm the results previously found that the E.M.F. created by light is independent of the cation.

VII. *The Effect of Covering the* Ag *Plates with Different Coatings of* AgBr *on the E.M.F. obtained.*

In the course of this research the same Ag plates had many times to be polished again, and covered afresh with AgBr. Surveying the E.M.F.'s obtained with freshly coated Ag-BrAg plates (when one of the two sides of each plate was covered with shellac and paraffin) in the same solutions at different times, there can be no doubt that there is no such thing as getting the same BrAg surface again. However well polished the plate may be, the AgBr surface is a conglomerate of crystals, which, according to the conditions of preparation (such as concentration of Br_2 in BrNa, time of action, temperature, &c.), are of a greater or smaller size, *i.e.*, in the same surface of the Ag plate different surfaces of the AgBr are exposed to light. We may call it "*physical variation of sensitiveness*" of the plates, similar to the phenomena observed with BrAg emulsions in the process of ripening.

VIII. Ag-IAg *Plates in* 0·1 *normal* KI *Solution* (*without solid* IK *on the Bottom of Quartz Vessel*) (*Plate* N20 *of February* 19, 1903), *Table VIII.*

In Table VIII. the investigation of the above system is given carried out with the arc between the 11th and 23rd of February, 1904. The direction of the current in the solution is always from the plate in the dark to the plate in light. The IAg plates were prepared in the dark through immersion of Ag plates (polished, as described before, and covered on one side with the shellac and paraffin) into a solution of iodine in potassium iodide. We find, as in case of Ag-BrAg plates, that the E.M.F. created by light of the same intensity first gradually increases (15th to 19th February), after previous illuminations it then reaches an apparent constant value, or even begins to decrease (18th to 23rd February). For the law of intensity we get (February 17, *with the blue screen*) less good results than with the weak acetylene light : $125^2 \times 45 = \mathbf{70{\cdot}3} \times 10^4$ and $92^2 \times 78 = \mathbf{66} \times 10^4$. The ratio of the deflections of the total light passing no screen to the total light passing the blue screen, the red screen, the yellow-green screen was found on February 15 to be 85·5, 35·4, 0, 0·5 or 100, 41·4, 0, 0·55 ; on February 17 : 117·6, 45, 0, 0·5 or 100, 38·5, 0, 0·045. The E.M.F. created by the total light passing the red screen cannot be measured, and that created by the total light passing the yellow-green screen is also very small, so as not to admit accurate measurement. It follows from this that the above E.M.F.'s given by the total light or the blue screen can be taken as created by light at a constant temperature. Plate of February 19 shows that the system represents a constant reversible cell. The reactions going on in the system are the same as those already discussed in § 5.

IX. *Plate* 15, *Table VII. The Transformation of Constant Reversible Cells into Inconstant Showing Polarisation, and vice versâ.*

The Ag-BrAg plates, which in different solutions of bromide were exposed to light during July, 1904 (see Table V.), began at last to show a very small polarisation. The Ag-BrAg plates were then kept in the dark in a 0·01 normal KBr solution. On November 18, 1904, a small polarisation was already very evident from the course of both the induction and deduction periods (see Plate N15, experimental data in Table VII.).

We remember that similar was the result with Ag-BrAg plates in a 0·1 normal NaBr solution on July 31, 1903 (see curve N9, especially N10 of plate N14), and with Ag-ClAg plates in NaCl solutions on July 1, 1903 (Table II.) after the plates were exposed for sufficient time to light. The differences (the total E.M.F.—E.M.F. of polarisation) were found here at 76 centims. distance: 73, 60 (corr. 71, the Swan a little shaky), 61 (corr. 72), 60 (corr. 75 millims.), *i.e.*, whether corrected or not, the E.M.F. of polarisation seems to be here for a given intensity (and composition) of light always of the same, or nearly the same value, as the principal E.M.F. is.

This transformation of the constant cells, after sufficient exposure to light, into inconstant, follows as a necessity from the kind of reactions going on in these systems and discussed in § 5. Since the current passes in these systems from the plate in the dark to the plate in light, the upper BrAg, ClAg layer of the exposed plate transforms into Ag, and the systems (Ag plate in light, BrNa solution, Ag-BrAg plate in the dark), &c., must be formed. A consideration of the reactions going on in such systems under the action of light, when the Ag plate is exposed to light, and direct experiments instituted with the system (Ag plate in light, BrNa solution, Ag-BrAg plate in the dark), showed that such combinations form inconstant cells, showing polarisation, thus confirming the kind of reactions going on in the system reversible in respect of the anion.

Moreover, a further consideration shows that we must be able to transform back the formed inconstant cell into the former constant cell, if we transform the formed under light Ag surface back into AgBr. This now is actually the case: by immersing the affected Ag-BrAg plate in a solution of Br_2 in water, &c., on several occasions I got back constant cells showing no polarisation.

X. *The Rôle of the Electrode. The System* Ag *Plates as Electrodes in Light and in the Dark,* BrAg *Solid at the Bottom of Cell and* 0·1 *normal* BrNa *Solution in Light and Dark. Polarisation* (*Plate N*24, *of July* 16, 1903. *Table IX.*).

The chemical composition of this system is the same as that of the systems previously dealt with (Ag-BrAg plates in BrNa solution) which is reversibly constant in respect of the anion; but the difference in reality proved to be very great. We find (see Plate N24 of July 16, 1903) that such a system behaves as the inconstant cell (Ag plates in BrNa solution), as is to be seen from the course of the induction and deduction periods, *i.e.*, the presence of the solid BrAg at the bottom of the vessel, without an intimate connection with the Ag plates so as to make it to an electrode does not make it to a constant cell (as if the solid AgBr were an extraneous substance). This puts into special light the rôle of the electrode under the action of light. Under the action of light the solution pressure of the electrode becomes, under given electrostatic conditions, greater, and it is the nature of this that determines the kind and nature of the galvanic cell created and the kind of reactions which can go on in it under the action of light. In one case (Ag-BrAg electrodes) $\overset{-}{Br}$ ions are passing from the electrode into the solution, in the other case the Ag plate could either send $\overset{+}{Ag}$ ions into the solution if it contains an Ag salt, forming a constant cell, or in the absence of an Ag salt in solution form, as in our case, an inconstant cell showing polarisation. As to the effect of light upon the chemical potential of the solid BrAg at the bottom of the cell, the same increases under the action of light, the solubility of AgBr may increase in light, though not to a measurable extent, more BrAg molecules may be sent into the solution, but this will be an ordinary and not an electrolytic solution, when $\overset{-}{Br}$ anions are passing into the solution.

Table IX., giving the experimental data for the above system, and Plate N24 show that the maximum deflection, or the maximum E.M.F.'s produced by light, does not remain constant, but first drops again owing to the further increase of the E.M.F. of polarisation under light. This goes on till a constant value of the E.M.F.'s is obtained, indicated by the lines (*d*) and giving the difference between the E.M.F. which light would have created, if there were no polarisation, and the E.M.F. of polarisation. As both E.M.F.'s are created simultaneously, the absolute values of both E.M.F.'s remain unknown.

For the constant deflections obtained with the light of the arc passing the *blue* screen, we get from N3 and 4: $80^2 \times 25·5 = \mathbf{163} \times 10^3$; $42^2 \times 72 = \mathbf{127} \times 10^3$. The value of the E.M.F. of polarisation thus seems to be in comparison with the principal E.M.F. small, since the law of intensity is still only partially obscured. Further we find that the arc (blue screen) gives much greater deflections than (total) acetylene (N4 : N11 or N12 = 72 millims. : 7·5 millims.), that the deflections got with the red and yellow-green screen are very small so as not to admit accurate measurement. It follows from this that in N1, 2, 3 and 4 the thermo E.M.F.'s are very small, so that E.M.F. is created by the total light or blue screen almost exclusively at a constant temperature. (The direction of the current will be discussed when inconstant cells will be dealt with.)

Similar were the results obtained with the system Ag plate in light, Ag-BrAg plate in the dark and BrNa solution. The matter at once becomes different where an intimate contact is established between the two parts which are to form the electrode, *e.g.*, when an insoluble mercury salt is in contact with liquid mercury, as we shall see later on.

XI. *The Systems* (Hg, *Solid* Hg_2Cl_2 *in* 0·1 *normal* NaCl *and* 0·1 *normal* KCl *Solution*), (Hg, *Solid* Hg_2Br_2 *in* 0·1 *normal* KBr *and* 0·1 *normal* NaBr *Solution*). *Plates N22 and N22′, Table X.*

The E.M.F. of the systems reversible in respect of the cation or anion is composed of the electrical potentials of the electrodes to the liquid in light and in the dark and of the electrical potential of the liquid in light to the liquid in the dark. The system Hg-Hg_2Cl_2 in 0·1 normal ClNa solution in light and in dark was investigated on July 25 and 26, 1904, and the system Hg-Hg_2Cl_2 in 0·1 normal KCl on July 27, 1904, both with acetylene at a distance = 88 centims. from quartz vessel (the light of Hg in the quartz vessel was about 2 centims.). No deflection could be established, at any rate it did not reach a millimetre. Plate N22 gives the photographic curve for ClNa. The system Hg-Hg_2Br_2 in 0·1 normal BrK and 0·1 normal BrNa was investigated with the arc at the distances of 118 and 47 centims. from the quartz vessel. No deflection was obtained (Plate N22′). This proves at the same time that not only does the electrical potential of Hg-Hg_2Cl_2 or Hg-Hg_2Br_2 to the solutions change in light exceedingly little, but *the electrical potential between the* ClNa *or* ClK *solution, or* BrK *or* BrNa *solution in the light and in the dark can only be exceedingly small, if at all measurable.*

Thus the proof is given that in the systems dealt with before, which are reversible in respect of the anion or cation, the variation of the osmotic pressure of the solution in light and resulting from its electrical potential between the solution in light and in the dark can be only very small, and that the last, in comparison with the electrical potentials of the plates to the solution in light and in the dark, is a negligible quantity.

XII. *What is to be understood under the "Electrode Reversible in respect of the Anion."*

In the consideration of the reactions going on in systems reversible in respect of the anion, we assume (with NERNST) that both Ag and ClAg or BrAg of the electrodes take part in the reversible reaction, the result of which is that the anion $\overline{\text{Cl}}$, $\overline{\text{Br}}$, &c., &c., either passes from the electrode into the solution or separates on the same, "as if" we had an electrode of "Cl," "Br," &c., behaving in a ClNa, BrNa solution as Zn or Cu in a $ZnSO_4$, $CuSO_4$ solution. This "as if" must be only taken as a useful illustration first introduced by NERNST for classification purposes. The electrode is a compound Ag-ClAg, Ag-BrAg and not a "Cl" or "Br" electrode, because otherwise the electrodes of all other combinations reversible in respect of the same anion ought to lead to the same values of the E.M.F. This however is not the case, as we see it from a comparison of the E.M.F.'s obtained with Ag-BrAg and $Hg\text{-}Hg_2Br_2$ in BrNa or BrK solution, obtained with Ag-ClAg and with $Hg\text{-}Hg_2Cl_2$ in the same ClNa solution. Thus we have in one case the compound Ag-ClAg electrode, in the other the compound $Hg\text{-}Hg_2Cl_2$ electrode, which are different, have a different solution pressure, a different electrical potential with the same solution, a different heat of reaction, though the *kind* of reaction going on in the system under the action of the current (transportation of $\bar{Cl}$, $\bar{Br}$ ions from one electrode to the other) is the same, and under the action of light the variation of the solution pressure and of the electrical potential of the different compound electrodes reversible in respect of the same anion to the same solution are different.

XIII. *The System* Hg, *Solid* Hg_2I_2 *in* IK *Solution* (*Table X.*). *The System* Hg, *Solid* SO_4Hg_2 *in Solutions of* SO_4Na_2, SO_4K_2, $SO_4(NH_4)_2$ (*Plate N°23, Table XI.*).

The first system could not be investigated, since Hg_2I_2 is decomposed by IK solution already in the dark; the second system could, since the Hg_2SO_4 is not decomposed by sulphates in the dark. The Hg_2SO_4 being very much more affected by light than Hg_2Cl_2, Hg_2Br_2, it was of special interest. In all investigations of the mercury cells the method was the same. The quartz vessel was divided into two compartments by fixing tightly into it an ebonite wall, 1 millim. thick, 2·7 centims. wide, circa 2 centims. high, with Crookes cement and then asphaltum, each compartment serving as an electrode. Mercury was first brought into the two compartments, then the solid SO_4Hg_2 (or Cl_2Hg_2, $Br_2\text{-}Hg_2$) over both mercury surfaces several millims. high, and then the solution on the top a few millims. over the ebonite partition. The mercury, solid salt and solution were mixed at the quartz windows of the vessel and SO_4Hg_2 entangled between the Hg and the quartz windows, so as to get vertical SO_4Hg_2 electrodes (besides SO_4Hg_2 being on the top). Two glass capillary tubes, sealed up at one end with long pieces of platinum wire leading from the closed ends and fixed in the ebonite top piece, were filled with mercury and the ebonite piece cautiously fixed in the quartz vessel. The heating of the HgPt junctions by light was thus as far as was practicable avoided.

It was soon found that the E.M.F. considerably changes with the quantity of mercury. The greater the amount of mercury (the vertical surface of SO_4Hg_2) the smaller the deflection—this is evidently due to the fact that the E.M.F. obtained is principally a thermo E.M.F. The E.M.F. obtained depends upon how the solid

SO_4Hg_2 was mixed up with the mercury. For this reason no comparative experiments with different systems can be made.

In all cases however we get constant cells, showing no polarisation, and the current always passed from the electrode in the dark to the electrode in light, as in all cells reversible in respect of the anion. Plate N23 gives an illustration of this for the system Hg, solid SO_4Hg_2 in 0·1 normal $SO_4(NH_4)_2$.

XIV. *On the Conditions under which a Constant Reversible Galvanic Cell can be realised under the Action of Light.*

It was explained before that according to the composition of the system and the reactions going on in the same, under the action of the current created by light, we get constant cells reversible in respect of the cation or the anion, or inconstant cells. We must however realise the following: the composition of the system and the reactions going on in the same under the action of the current give here, as in ordinary galvanic cells, the conditions of constancy and reversibility *only in general*, but in no galvanic combination we know of does the principal reversible reaction, upon which the constancy of the cell depends, take place alone to the entire exclusion of all other phenomena and reactions simultaneously taking place in the galvanic cell. A constant reversible galvanic cell is in all cases only "practically" reversibly constant. To start with, there are no two electrodes (even when highly polished) made of the same metal, which do not give an E.M.F. in the dark when connected to a circuit. Therefore no two galvanic cells of the same combinations can give the same E.M.F. In the next instance, it is well known that, to keep the E.M.F. of a constant reversible for any length of time practically constant, only small currents must be used. The reason of this is that, besides the principal reaction under the action of the current, subsidiary reactions take place which become more prominent the greater the current density; these reactions also lead to the formation of gas batteries, or attack the electrodes, &c. In the third instance, there are very few metals which can be got chemically pure (absolutely pure perhaps none), and this leads to local currents, local E.M.F., &c. In the fourth instance, there is a variation of concentration at the electrodes. In ordinary constant reversible galvanic cells the principal E.M.F.'s of the principal reversible reaction, due to the composition of the system, happen to be, in comparison with the interfering E.M.F.'s, very great, since the difference in the electrical potentials of the electrodes, consisting of two entirely different metals or combinations, to the solution are great—hence ordinary constant cells can practically be easily realised. When, however, we pass to galvanic cells created by light, where the E.M.F.'s created by light, in connection with the composition of the same, are very small, it is evident that the difficulties for a practical realisation of constant cells must become enormous.

The above fixes the problem and also shows the limit of possible success in this region. Only where the solution pressure of the plate increases in light essentially, so that a comparatively great E.M.F. is created, can we realise, under proper conditions, constant reversible cells, *e.g.*, in case of Ag-ClAg, Ag-BrAg in ClNa, BrNa solution, or Cu-CuO in NaOH solution. As, however, the E.M.F. created by light is always very small, special care will always have to be taken for a corresponding reduction of the other interfering E.M.F.'s, to an extent not known for ordinary galvanic cells: (1) the E.M.F. in the dark must first be reduced by special polishing of the plates, by mechanical means and with the current, to a few hundred thousandths of a volt. On such plates usually, but not always, also very little gas separates while the current is passing between the plates under the action of light. Only very few metals allow such a polishing. The rougher the grain of the metal or the thicker the deposited compound is, the more difficult is the realisation of the same. (2) Only chemically pure metals or compounds should be used as electrodes. This can be realised in case of Ag, Pt, Au, Hg, Ag-ClAg, AgBrAg, Ag-I-Ag, Hg with insoluble Hg salts, and perhaps in one or two more cases, but it is a matter of quite extraordinary difficulty in case of other metals. (3) The currents used should be made, as corresponds to this region, very small by inserting, when possible, resistances into the circuit, and using a very sensitive galvanometer.

In addition to the above conditions, which are common for all galvanic cells, a series of further conditions and possibilities is never to be lost sight of, which are important for this region only, such as the formation of thermo E.M.F.'s in the circuit, the variation of the sensitiveness of the plates to light in the dark, the effect of previous illumination, the character of the induction and deduction periods, the transformation of one system into another, &c., &c., which can be mastered only after a detailed and careful study of each system separately is made.

XV. *On the E.M.F.'s of Constant Reversible Cells and the Intensity of Light.*

Becquerel found with Ag-Ag_2Cl plates in a solution of 2 grammes of SO_4H_2 in 100 grammes water ('La Lumière,' vol. II., p. 145), that the E.M.F. is not directly proportional to the intensity of light, since the product I.H. is not constant. The result obtained by Minchin with his sensitised cell, consisting of Sn plates covered (evidently) with SnO_2 in methyl-alcohol, is different. The E.M.F. was "with fair accuracy found to be inversely proportional to the distance" of the candle from the cell, *i.e.*, the intensity is directly proportional to the square root of the intensity of light.

Contrary to these observations, I found that with constant reversible cells (*i.e.*, cells the E.M.F. of which gives the true measure of the maximum work performed under the action of light) the E.M.F. is directly proportional to the intensity of light. The reasons of this discrepancy are:

(1) The system Ag-Ag_2Cl in a solution of SO_4H_2 and the system Sn-SnO_2 in

alcohol are inconstant cells, showing polarisation, *i.e.*, the E.M.F. does not give the maximum work performed under the action of light.

(2) If only strips of the front plate are illuminated (Becquerel), local action takes place between the illuminated and non-illuminated parts of the front plate.

(3) In their publications no data are given to show how far the E.M.F.'s in the dark were brought in their experiments not only to constant, but also to sufficiently small values; the thermo E.M.F.'s in the cell, &c., do not seem to have been sufficiently guarded against. They did not possess a constant source of light, nor measure and check the intensity of their source of light, or take into account the induction and deduction periods. We have no evidence as to how far they reached the constant maximum deflections in each case—this is not always easily obtainable—nor how far the E.M.F. in the dark was influenced during their experiments by previous exposure of the system to light, &c., &c.

§ 8. *Experimental Proof of the Physico-Mathematical Theory of "Constant Reversible Cells Created by Light" (given by the Author in 'Roy. Soc. Proc.,' November*, 1904).

In the above paper the same was dealt with by the author in detail. The general equation found was

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860\,T\left(\log_e \frac{Pl}{Pd} - \frac{2v}{u+v}\log_e \frac{pl}{pd}\right)\cdot 10^{-4} \text{ volt}$$

for systems reversible in respect of the cation, and

$$\Sigma E = E_1 + E_2 - E_3 = 0{\cdot}860\,T\left(-\log_e \frac{Pl}{Pd} + \frac{2u}{u+v}\log_e \frac{pl}{pd}\right)\cdot 10^{-4} \text{ volt}$$

for systems reversible in respect of the anion.

The present research confirms the conclusions drawn there from the above equations:—

(1) Table IV., Plates 30 of July 31, 1903, August 1, 1903, prove for the cells reversible in respect of the anion; experiments of June 19, 1903, § 6, Plates 7, 8, 9, Table I., prove the cells reversible in respect of the cation, that E.M.F. is independent of concentration.

(2) Experiments, § 7, XI., Table X., Plates N22 and N22′, of the 25th to the 27th of July, 1904, and of February 27, 1905, as well as § 7, XI., Table X., show that both the value

$$0{\cdot}860T\,\frac{2v}{u+v}\log_e \frac{pl}{pd}\cdot 10^{-4} \text{ volt, or } 0{\cdot}860T\,\frac{2u}{u+v}\log_e \frac{pl}{pd}\cdot 10^{-4} \text{ volt,}$$

and the electrical potential between the illuminated and non-illuminated parts of the solution can be neglected, so that instead of (I) we can use

$$\Sigma E = 0{\cdot}860T\log_e \frac{Pl}{Pd}\cdot 10^{-4} \text{ volt, and } \Sigma E = 0{\cdot}860T\log_e \frac{Pd}{Pl}\cdot 10^{-4} \text{ volt.}$$

(3) Through this the indirect experimental proof is given that

$$n_e\epsilon_0\Sigma E = \rho'' + \frac{n_e\epsilon_0\, d\Sigma E}{dT} \,.\, T,$$

i.e., a law analogous to that of GIBBS-HELMHOLTZ for ordinary cells holds good for galvanic cells created by light. The experiments (given in § 7) of the 8th till the 13th of July, 20th of July, 1904, and of the 15th of February, 1905, Plate 19, Table V., show, however, that there are enormous difficulties in this region of research to determine the value of

$$\frac{n_e\epsilon_0\, d\Sigma E}{dT} \,.\, T,$$

experimentally, the value having proved to be too small for experimental determination in view of other sources of error.

(4) The heat of reaction ρ'', or the difference of the heats of ionisation in light and in the dark can, for the same reason, be determined experimentally only approximately by putting $\rho'' = n_e\epsilon_0\Sigma E$. *The heat of reactions evidently changes as the E.M.F. does, both with the intensity and composition of light*, which is quite a characteristic feature for galvanic cells created by light. The heats of reaction are always exceedingly small, as the E.M.F.'s are. Thus the heat of reaction for one electro-chemical equivalent of $\bar{\text{Br}}$ ions in the system (Ag-BrAg plates in 0·1 norm. NaBr solution) giving, *e.g.*, 106×10^{-6} volt $= 23040 \times 106 \times 10^{-6} =$ **2·442 gram. cal.** (see § 7, p. 365). The systems, Ag plates in NO_3Ag solution, gave E.M.F.'s between $1·8 \times 10^{-6}$ volt and $54·4 \times 10^{-6}$ volts. The value of ρ'' for 1 electro-chemical equivalent of Ag ions is thus $= 23040 \times (1·8 \text{ to } 54·4) \times 10^{-6} =$ **0·044 to 1·25 gram. cal.** (see § 6, p. 355).

(5) This research (§ 6, § 7, II. and XV.) shows that *the solution pressure of the electrodes in light* is *sui generis*, since it *changes, as well as the E.M.F., with the intensity of light and its composition.* Experiments of § 7, II. and X., show also the effect of the capacity of the plates for absorption of light, the effects of previous illuminations, of physical changes in the dark, upon E.M.F. obtained, and consequently upon the solution pressure and heat of reaction of some systems.

As to the variation of the solution pressure of an electrode on exposition to light, experiments show that it is very small: thus, in case of the system (Ag-BrAg plates in BrNa solution) giving 106×10^{-6} volt, we get

$$\log\frac{Pl}{Pd} = \frac{106 \times 10^{-2}}{0·860T \times 2·306}\text{; at } T = 290^\circ\ (17^\circ\text{ C.}) : \log\frac{Pl}{Pd} = 0·001846 \text{ and } Pl\ 1·0043Pd,$$

i.e., an increase of the solution pressure by 0·43 per cent. For Ag plates in NO_3Ag solutions, giving (for different intensities) E.M.F.'s from $1·8 \times 10^{-6}$ volt to $54·4 \times 10^{-6}$ volt, we get for

$$T = 290^\circ\text{ C. : } \log Pl/Pd = 0·000031 \text{ to } 0·00095,\quad Pl = 1·00072 \text{ to } 1·0022Pd,$$

an increase by 0·0072 per cent. to 0·22 per cent. If the solution pressure of an electrode in the dark is known, the solution pressure in light, under any given condition, is also known. Putting Pd for $Ag = 10^{-15}$ atmosphere, the solution pressure of Ag plates becomes in light in the investigated systems

$$Pl = (1{\cdot}00072 \text{ to } 1{\cdot}0022)\ 10^{-15} \text{ atmosphere.}$$

(6) § 7, I., II., VIII., XV., as well as Table I., § 6, show that in constant reversible cells the E.M.F. created by light, and with it approximately the heat of reaction, are directly proportional to the intensity of light, *i.e.*, $\Sigma E = CI$; $\rho'' = C'I$, and since the same holds good for plates absorbing the total light (CuO in NaOH) and for plates absorbing only a part of it (Ag plates in NO_3Ag), the same law of intensity holds good (at any rate approximately) for the absorbed, as well as for the reflected light. Experiments of July 29, 1903, Plate N13, Table III., carried out with pure red light, and § 7, VIII., with blue light, show that the same law of intensity holds good for monochromatic light as well.

§ 9. *The Results obtained for Chemical Statics and Dynamics under the Action of Light, in General.*

(*a*) *Further Experimental Proof that Velocity of Chemical Reaction in Homogeneous Systems when they are shifted to a New Point of Equilibrium by Light at a Constant Temperature, and Chemical Equilibrium of Homogeneous Systems, follow the Laws of Mass Action as in the Dark.*

The above laws which I found experimentally to regulate, after the induction period has passed, those regions of phenomena under the action of light (see 'Roy. Soc. Proc.,' January, 1902; 'Phil. Trans.,' A, 1902, vol. 199, p. 337; 'Zeitschr. für physik. Chemie,' June and December, 1902; 'Phil. Mag.,' January, 1903) now find further extensive experimental confirmation in the "galvanic cells created by light" as is evident from (*c*).

Having shown here that the chemical potential of the same plate is in light different from that in the dark, the proof is thus given that the thermodynamic deduction of the same laws of mass action (after the induction period) given in the above papers is a mathematical necessity.

Since the publication of the papers above mentioned, a series of efforts have been made by different persons to investigate velocity of reaction, or velocity of reaction and equilibrium under the action of light, but with little success (see Guldberg, 'Zeitschr. physik. Chemie,' 41, 1902; Slator, 'Zeitschr. physik. Chemie,' 45, p. 540, 1903; P. Bevan, 'Phil. Trans.,' A, 1904; Luther and Weigert, 'Sitz. K. Preuss. Akad.,' 1904, p. 828).

No reference was made in the above publications to my work. The cause of failure is not far to seek; in all the above researches the reactions used are either of a compound character (Cl_2 and H_2) or they do not admit a quantitative investigation (Anthracen and Dianthracen); the authors possessed no constant source of light and no photometer for measuring its intensity, take no account of the induction (except BEVAN) and deduction periods, nor of the very great number of sources of error one meets in this region.

(b) *Experimental Proof that Chemical Equilibrium in Heterogeneous Systems, when Shifted by Light at a Constant Temperature to a New Point, follows, after the Induction Period has passed, the same Laws as in the Dark.*

Since the E.M.F. of the reversible heterogeneous system forming the galvanic cell gives, after the induction period has passed, the maximum work performed in it under the action of light, and since the equations giving the maximum work under the action of light contain also the constant of chemical equilibrium of the heterogeneous system, as in ordinary galvanic cells, an experimental proof is thus given that chemical equilibrium in heterogeneous systems follows, under the action of light (after the induction period has passed) the same laws as in the dark. In the 'Zeitschr. physik. Chemie' (vol. 30, pp. 371–382, 1899) I showed that the laws of GULDBERG and WAAGE and others, for equilibrium of ordinary heterogeneous systems, must be conceived as the result of a combination of static equilibria between the different parts of the heterogeneous system and of dynamic equilibria in the homogeneous parts, and that it is the form of the last which determines at the same time the form of GULDBERG-WAAGE's laws. The present research, dealing with heterogeneous systems, gives us for this reason at the same time also experimental proof that equilibrium in homogeneous systems, and with it velocity of reaction, follows in light, after the induction period, the laws of mass action.

(c) *The Maximum Work (Constant of Equilibrium) and the Law of Intensity of Light.*

We have found that the E.M.F. or maximum work done under the action of light in the reversible heterogeneous systems forming the galvanic cells is, after the induction has passed, directly proportional to the intensity of light.

This must therefore hold good, after the induction period, also for the maximum work done under the action of light in homogeneous system, *i.e.*,

$$\mathrm{RT}\log_e \frac{C_1^{N_1}C_2^{N_2}}{C_3^{N_3}C_4^{N_4}} = \mathrm{RT}\log_e \frac{K_1}{K_2} = \mathrm{RT}\log_e K = CI_1 \quad . \quad . \quad . \quad . \quad (\alpha),$$

where $C_1, C_2 \ldots C_3, C_4 \ldots$ are the concentrations of the substances taking part in the opposite reactions, K_1, K_2 the velocity constants of the two opposite reactions, K the constant of equilibrium. This law giving the connection between the constant of equilibrium, absolute temperature, and the intensity of light (given first by the author in the 'Zeitschr. für physik. Chemie,' 1902, vol. 42, pp. 319, 333, 'Phil. Mag.,' 1903, (6), pp. 211, 214), is thus amply verified on several systems in this research.

(*d*) *On the Connection between the Velocity of Chemical Reaction produced by the Action of Light, the Intensity of Light and Absolute Temperature.*

From the above equation (α) it follows :—

(a) When both opposite reactions go on under the action of light only :

$$\mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I} \text{ or } \mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I}+(\mathrm{K}) \text{ and } \mathrm{RT}\log_e \mathrm{K}_2 = \mathrm{C}'''\mathrm{I}$$
$$\text{or } \mathrm{RT}\log_e \mathrm{K}_2 = \mathrm{C}'''\mathrm{I}+(\mathrm{K}).$$

(b) If only one of the reactions goes on under the action of light, while the other opposite one goes on also in the dark (and its velocity is not influenced essentially by light)

$$\mathrm{RT}\log_e \mathrm{K}_1 = \mathrm{C}''\mathrm{I}+\mathrm{RT}\log_e \mathrm{K}_{\mathrm{II}}.$$

At a constant temperature

$$\log_e \mathrm{K}_1 = \mathrm{C}'^{\mathrm{V}}\mathrm{I}+\mathrm{K}_{\mathrm{IV}}.$$

The above gives the true law for the connection between the velocity constant of chemical reactions produced by light, the intensity of light and the absolute temperature (after the induction period has passed).

(*e*) *The Velocity of Molecular or Physical Reactions between different parts of the Heterogeneous System produced by and going on only under the Action of Light evidently follows the Law found by the Author for these Reactions in the Dark.*

The equations found experimentally by the author for the induction and deduction periods $\frac{d\pi}{d\tau} = c\,(\pi'_0-\pi)\,(\pi-\pi_0+\mathrm{K})$ and $-\frac{d\pi}{d\tau} = -c'\,(\pi_0-\pi)\,(\pi-\pi'_0+\mathrm{K}')$ (see 'Proc. Roy. Soc.,' vol. 74, 1904, p. 369) give the speed of transformation of a substance (Ag, AgBr, Cu, &c.) from its state of equilibrium with its ions in solution in the dark to its state of equilibrium with its ions in light and *vice versâ*. They correspond both in form and content to the general equation $\frac{dt}{d\tau} = c\,(t_0-t)\,(t-t_{0v}+\mathrm{K})$, or $\frac{dt}{d\tau} = c\,(\Sigma+\mathrm{K})\,(t_0-t)$, which, as I established experimentally, is giving the speed of all molecular or physical reactions between different parts of the heterogeneous system in the dark.

A full account of my investigations was given in the 'Report of the British Association,' Liverpool, 1896. Since 1896 I often made use of the above results in many of my publications (see 'Report Brit. Ass.,' Liverpool, 1906, the 'Zeitschr. physik. Chemie,' vol. 30, pp. 348–368, 1899, 'Phil. Mag.,' July, 1901, pp. 50–90). The very same equation (and for the same kind of reaction) later on NOYES and WHITNEY ('Zeitschr. physik. Chemie,' vol. 23, p. 689, 1897), and more recently NERNST and BRUNNER ('Zeitschr. physik. Chemie,' vol. 47, pp. 50–102, 1904), confirmed in their investigations of the speed of solution of salts. The equation used by NOYES and WHITNEY (using the same notation) is $\frac{dt}{d\tau} = c' (t_0 - t)$ (they are taking the velocity constant per unit surface); the equation used by NERNST and BRUNNER is $\frac{dt}{d\tau} = \frac{D}{\delta} \Sigma_t (t_0 - t)$ or $= C\Sigma_t (t_0 - t)$, where $\frac{D}{\delta}$ is also a constant as my C is. So far they only confirm the general law which was given and established by me before NOYES and WHITNEY, and long before NERNST and BRUNNER (also for solution and separation of salt, &c., &c.).

As to their attempt to explain the constant C by diffusion, it entails a number of hypotheses, which appear to me to be quite incompatible with experience. As none of their fundamental hypotheses have been, in my opinion, shown to exist by any reliable experiments, they seem to me at present only as arbitrary interpretations of qualitative results. My law has been shown to be general, it gives the velocity of *all* molecular transformations between different parts of the heterogeneous system, including those (such as melting of ice, separation of ice from overcooled water, &c.) where diffusion cannot possibly enter into consideration. It follows, therefore, that a law of such a wide scope cannot be based upon diffusion, and that no more should be read in the content of my equation than it is clearly given by its form.

(*f*) *Velocity of Chemical Reaction in Heterogeneous Systems, produced by and going on only under the Action of Light, evidently follows after the Induction Period has passed, the Laws deduced by the Author for Velocity of Chemical Reaction in Heterogeneous Systems in the Dark.*

We have thus shown, on the one hand, that the velocity of chemical reaction in homogeneous systems under the action of light follows, after the induction period, the law of mass action, as in the dark, and, on the other hand, the equations for the induction and deduction periods in galvanic cells make it highly probable that the speed of molecular or physical transformations between different parts of the heterogeneous system under the action of light must follow the same law as in the dark. It follows from this that the laws governing velocity of chemical reaction in heterogeneous systems under the action of light, must, after the induction period has passed, follow the laws which I deduced for this region in the dark. In 'Zeitschr. physik. Chemie,' 1899, vol. 30, pp. 371–382, and 'Phil. Mag.,' 1902 (6) 4, pp. 468–489, I showed that the laws for velocity of chemical reaction in heterogeneous systems follow (in the dark), as a mathematical necessity, from two well-established laws—one governing the speed of reaction in homogeneous parts of the system (the law of mass action) and the other the speed of molecular reactions (speed of solution or evaporation and of separation or condensation of solids or liquids in the system) between the different parts in the system (a law established by myself). After the work of HELMHOLTZ and PLANCK, and others who find themselves constrained to assume that every substance has a solution pressure or vapour pressure, in order to explain the phenomena of formation of electrical potential in a galvanic combination, &c., the above treatment of the subject becomes an unavoidable necessity.

Messrs. NERNST and BRUNNER therefore should not have applied a law which I established for molecular reactions between the same substance in different parts of the heterogeneous system to the velocity of chemical reaction in heterogeneous systems, which is a conglomerate of reactions. The reactions investigated by NERNST and BRUNNER are only particular instances of my laws and equations for chemical reactions in heterogeneous systems, and any conceivable values may be taken for each member of the equations without impairing in the least degree their validity. If the numerous assumptions of NERNST and BRUNNER be true, they must therefore follow as a particular case of my equations; but, as I will show at another place, both their assumptions and experiments are arbitrary.

In conclusion I wish to express my thanks to the Managers of the Royal Institution for enabling me to make use of the resources of the Davy-Faraday Laboratory, and especially to Dr. LUDWIG MOND, who by his kind assistance and interest in my work enabled me to undertake and to carry out the above research.

TABLE I.—Ag Plate in Light, $AgNO_3$ Solution in

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
2	Ag in light and in dark	0·25 normal $AgNO_3$	June 3 and 4, 1903	1·5 centims. to right	15·0	1, 2, 3, 4, 5, 6	20, 19, 17, 18, 18, 16 = average 18	13·4	847·8
							corr. 20, 21, 19, 20, 20, 18 = average 19·7	13·4	847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	7, 8, 9, 10, 11, 12	24, 24, 26, 24, 23, 23·5 = average 24	13·4	847·8
							corr. 24, 26, 26, 26, 26, 26·5 = average 25·8	13·4	847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	13	compound curve	13·4	847·8
	ditto	ditto	June 3 and 4, 1903	ditto	15·0	14, 15, 16	21, 21, 21 = average 21	13·4	847·8
							corr. 24, 24, 24 = average 24	13·4	847·8
3	ditto	ditto	June 5, 1903	ditto	15·0	1, 2, 3, 4	36, 35, 34, 33 = average 34·5	13·4	847·8
							corr. 36, 37, 37, 36 = average 36·5	13·4	847·8
	ditto	ditto	June 5, 1903	ditto	15·0	5, 6, 7, 8, 9	17, 15·7, 17, 19, 17 = average 17	13·4	847·8
4	ditto	ditto	June 6, 1903	8·5 centims. to right	84·8	1, 2	55, 54 = average 54·5	13·4	847·8
	ditto	ditto	June 6, 1903	ditto	84·8	3, 4	28, 28 = average 28	13·4	847·8
5	ditto	ditto	June 8, 1903	9·5 centims. to right	94·8	1, 2, —, 4	29, 29, —, 26 (7) = average 28·2	13·4	847·8
6	ditto	ditto	June 11, 1903	2·7 centims. to right	27·0	1	32	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	2	15	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	3, 3′	2·5	13·4	847·8
	ditto	ditto	June 11, 1903	ditto	27·0	4, 4′	1·75 *	13·4	847·8
—	ditto	0·0041 normal $AgNO_3$	June 18, 1903	17 centims. to right	27·0	1	20·5	840	1674
7	ditto	0·0041 normal $AgNO_3$	June 19, 1903 (*a*)	1·9 centims. to left	38·2	(1), 2, 3	10·5, 10 = average 10·25	840	1674
	ditto	ditto	June 19, 1903 (*a*)	ditto	38·2	4, 5	19, 18 = average 18·5	840	1674
8	ditto	0·025 normal $AgNO_3$	June 19, 1903 (*b*)	1·0 centim. to left	10·3	1, 2, 3	40·5, 34·5, 38 = average 37·3	146	980·4
	ditto	ditto	June 19, 1903 (*b*)	ditto	10·3	4, 5	23·5, 21·5 = average 22·5	146	980·4
9	ditto	0·25 normal $AgNO_3$	June 19, 1903 (*c*)	0·9 centim. to left	9·0	1, 2	40, 40 = average 40	16·5	851·9
	ditto	ditto	June 19, 1903 (*c*)	ditto	9·0	3, 4	26, 21 = average 23·5	16·5	851·9

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* The temperature *of the bath and of the room* were those of

Light, AgNO$_3$ Solution in Dark, Ag in the Dark.

verage mpères bserved in 10^{-9} units. XI.	Average volts observed in 10^{-6} units. XII.	Calibration of Nalder N1, in centimetres (right and left). XIII.	Calibration of Nalder N2, in centimetres (right and left). XIV.	Distance of light from quartz vessel, in centimetres. XV.	Distance of light from Rubens thermopile, in centimetres. XVI.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left). XVII.	Temperature of bath, in ° C. XVIII.	Temperature of room, in ° C. XIX.	Kind of cell. XX.	Kind of light used. XXI.	Volts and ampères when arc was used. XXII.	Photographic plate number.
21·1	18·0	17·4	19·8	37	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	2
23·1	19·6	—	—	—	—	—	—	—	—	—	—	
28·1	24·0	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
30·2	25·7	—	—	—	—	—	—	—	—	—	—	
—	—	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
28·1	24·0	17·4	19·8	33	110	116	17·5	17·5	constant	total light	arc: 65 volts, 6 ampères	
32·1	27·4	—	—	—	—	—	—	—	—	—	—	
40·5	34·4	17·4	19·8	26	110	121	ordinary temperature*		constant	total light	arc: 65 volts, 6 ampères	3
42·8	36·4	—	—	—	—	—	—		—	—	—	
19·0	16·9	17·4	19·8	36 (7)	110	115	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
63·9	54·4	17·4	19·8	26	110	127	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	4
32·8	27·9	17·4	19·8	36	110	127	ordinary temperature		constant	total light	—	
33·0	28·1	17·4	19·8	36	110	135	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	5
37·5	31·9	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	6
17·6	15·0	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	blue screen	arc: 65 volts, 6 ampères	
2·9	2·4	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	yellow green screen	arc: 65 volts, 6 ampères	
2·1	1·8	18·3	19·8	36 (7)	110	129	ordinary temperature		constant	red screen	arc: 65 volts, 6 ampères	
—	—	—	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	—
12·3	20·6	17·4	17·2	36 (7)	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	7
21·7	36·3	17·4	17·2	26 (7)	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
43·6	38·4	17·4	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	8
26·3	23·2	17·4	17·2	37	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	
46·9	39·8	17·4	17·2	27	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	9
27·6	23·4	17·4	17·2	37	110	112	ordinary temperature		constant	total light	arc: 65 volts, 6 ampères	

ordinary temperature of the room, *i.e.*, between 17°·5 and 20° C.

TABLE II.—Ag-ClAg Plates in

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volt.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
10	Ag-ClAg in light and in dark	0·1 normal NaCl	June 30, 1903	5·0 centims. to right	46·2	1, 2	56, 53 (corr. 55) = average 55·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	3, 4	31, 34 = average 32·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	5, 6	3·5, 3·5	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	7, 8	13, 13	44·5	878·9
	ditto	ditto	June 30, 1903	ditto	46·2	10	5·5	44·5	878·9
	ditto	ditto	July 1, 1903	0·13 centim.	12·1	1, 2, 3, 4, 5	(53·5), 66·1, 68·3, 68·3, 70 = average 68·2	44·5	878·9

TABLE III.—Ag-BrAg Plates in

11	Ag-BrAg in light and in dark	0·1 normal NaBr	July 28, 1903	18 centims. to left	16·7	1, 2, 3	49, 44–45, 45–46 = average 46·3	43	877·4
12	ditto	ditto	July 29, 1903	1·5 centims. to right	14·2	1, 2 3, 4, 5	84, 88, 82, 80, 81 = average 81·6	43	877·4
	ditto	ditto	July 29 1903	ditto	14·2	6, 7	43·5, 44·5 = average 44	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	8, 9	32·5, 31·0 = average 31·8	43	877·4
13	ditto	ditto	July 29, 1903	ditto	14·2	1	80	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	2, 3	28, 29, = average 28·5	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	4	60	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	5	118	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	6	48·5	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	7	41	43	877·4
	ditto	ditto	July 29, 1903	ditto	14·2	8, 10, 14	76, 69, 71·5	43	Resistance of galvanometer = 834·4 ohms shunt of galvanometer = 40 ohms
	ditto	ditto	July 29, 1903	ditto	14·2	15	120	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	9	23	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	11	5	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	12	3·5	43	ditto
	ditto	ditto	July 29, 1903	ditto	14·2	13	64·5	43	ditto

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* Formation of the system Ag in the light NaCl solution, Ag-ClA

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI, in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
0·1 Normal NaCl Solution.												
59	51·8	19·2	16·7	37	110	155	20	20	constant	total light	arc: 65 volts, 6·0 ampères	10
34·6	30·4	19·2	16·7	50	110	155	20	20	constant	total light	arc: 65 volts, 6·0 ampères	
3·7	3·3	19·2	16·7	37	110	155	20	20	constant	red screen	arc: 65 volts, 6·0 ampères	
13·8	12·1	19·2	16·7	37	110	155	20	20	constant	blue screen	arc: 65 volts, 6·0 ampères	
5·8	5·1	19·2	16·7	37	110	155	20	20	constant	yellow-green screen	arc: 65 volts, 6·0 ampères	
72·5	63·6	19·2	16·7	37	110	155	20	20	beginning of polarisation*	total light	arc: 65 volts, 6·0 ampères	
0·1 Normal NaBr Solution.												
49·2	43·4	19·2	17·0	116	110	61	ordinary temperature†		constant	total light	acetylene	11
86·7	76·1	19·1	17·05	116	110	71	ordinary temperature		constant	total light	acetylene	12
46·8	41·0	19·1	17·05	116	110	39	ordinary temperature		constant	total light	acetylene	
33·8	29·6	19·1	17·05	116	110	28·5	ordinary temperature		constant	total light	acetylene	
85·0	74·7	19·1	17·05	116	110	64·6	ordinary temperature		constant	total light	acetylene	13
30·3	26·6	19·1	17·05	116	110	64·6	ordinary temperature		constant	red screen	acetylene	
63·7	55·9	19·1	17·05	80	110	64·6	ordinary temperature		constant	red screen	acetylene	
125·3 to 126·4	110 to 111	19·1	17·05	57	110	64·6	ordinary temperature		constant	red screen	acetylene	
51·6	45·3	19·1	17·05	80	110	64·6	ordinary temperature		constant	blue screen	acetylene	
43·6	38·3	19·1	17·05	80	110	64·6	ordinary temperature		constant	yellow-green screen	acetylene	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	total light	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	89	92	64·6	ordinary temperature		constant	total light	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	blue screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	red screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	yellow-green screen	arc: 70 volts, 6·2 ampères	
—	—	19·1	17·05	118	92	64·6	ordinary temperature		constant	colourless gelatine	arc: 70 volts, 6·2 ampères	

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in the dark.

† Temperature of bath and of room, 17°·5 C. to 20° C.

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.

TABLE IV.—Ag-BrAg Plates in NaBr

14	Ag-BrAg electrode in light and in dark	from 0·1 normal to circa 0·01 normal NaBr	July 30, 1903	1·3 centims. to left	12·1	1, 2 (*a*)	114, 113·5	43·4	877·4
	ditto	ditto	July 30, 1903	6·0 centims. to left	61·8	3, 4 (*b*)	114, 116	137	971·4
	ditto	ditto	July 30, 1903	14 centims. to right	183·5	5, 6 (*c*)	80, 86	400	1234·4
	ditto	from circa 0·1 normal to circa 0·025 normal NaBr	July 31, 1903	0·3 centim. to left	2·8	(7), 8 (*a*′)	(123), 120	50	884·4
	ditto	ditto	July 31, 1903	14 centims. to left	125·0	9, 10 (*b*′)	105, 106	5	839·4
	ditto	ditto	July 31, 1903	7 centims. to right	74·2	11, 12 (*c*′)	92, 99	163·4	950·8
Scale on the drum of chronograph.	ditto	0·025 normal NaBr	August 1, 1903	1 centim. to left in 13, 14, 6·5 centims. to left in 15	10·4 in 13, 14, 5·2 in 15	13, 14, 15	105, 104·5, 106	142·9	977·3

TABLE V.—Ag-BrAg Plates in Decinormal KBr Solution and LiBr Solution. Influence of Tempe

	Ag-BrAg plates in light and in dark	0·1 normal KBr	July 8, 1904	0·5 centim. to right (no shunt)	—	1, 2	75·4, 75·4	17·9	Resistance of galvanometer =834·4; the galvanometer is shunted with 200 ohms
	ditto	ditto	July 8, 1904	ditto	—	3, 4	81·7, 81·7	17·9	ditto
	ditto	ditto	July 9, 1904	0·6 centim. to right (no shunt)	—	1, 2	107, 108	17·9	ditto
	ditto	ditto	July 9, 1904	ditto	—	3, 4	102, 101	17·9	ditto
	ditto	ditto	July 13, 1904	5·5 centims. to right	—	1, 2	133, 133	17·9	ditto
	ditto	ditto	July 13, 1904	1·7 centims. to right	—	3, 4	136, 133	17·9	ditto
	ditto	ditto	July 13, 1904	1·5 centims. to right (200 ohms shunt)	—	5, 6	140, 136	17·9	ditto

From the 15th till the 19th of July the Ag-BrAg plates were in HBr solutions. This made the deflections gradually smaller: temperature on these plates was again tested. A 0·1 normal

	Ag-BrAg in light and in dark	0·1 normal LiBr	July 20, 1904	1·9 centims. to right	—	1, 2	126, 125	—	ditto
	ditto	ditto	July 20, 1904	0·3 centim. to left	—	3, 4, 5	117·5, 125 corr., 125 corr.	—	ditto

On the 15th of February, 1905, the influence of temperature again tested with plates newly covered; one side of

19	Ag-BrAg	0·1 normal NaBr	February 15, 1905	18·3 centims. to left	—	1	85	17·70	852·1
	ditto	ditto	February 15, 1905	ditto	—	2	87·5	17·70	852·1

verage mpères bserved in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	

Solutions. Influence of Concentration.

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
120	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	14
122	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
88	106	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetyleno	
127·5	112·7	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
112	94	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
101·5	101·2	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	
111·7	109·1	19·1	17·0	116	110	67	ordinary temperature		constant	total light	acetylene	Scale on the drum of chronograph.

rature. (Both sides of the Ag Plates covered with AgBr; Glass Vessel instead of Quartz Vesssel.)

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
—	—	17·0	16·0	89	123	48·5	**38·1**	ordinary temperature	constant	total light	acetylene	
—	—	17·0	16·0	89	123	48·5	**20·8**	ditto	constant	total light	acetylene	
—	—	17·2	16·05	89	123	48·8	**2·8**	ditto	constant	total light	acetylene	
—	—	17·2	16·05	89	123	48·8	**27·1**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**48·5**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**33·5**	ditto	constant	total light	acetylene	
—	—	17·2	16·03	89	123	45·5	**2·3**	ditto	constant	total light	acetylene	

from 140, 136 millims. to 65 millims., for reasons to be explained in another place. On the 20th July the influence of LiBr solution (with 200 ohms. shunt of galvanometer) gave :—

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
—	—	16·0	16·2	89	123	46·5	**23**	ditto	constant	total light	acetylene	
—	—	16·0	16·2	89	123	46·5	**3**	ditto	constant	total light	acetylene	

each electrode was covered with shellac and paraffin. NaBr solution was taken. No shunt with galvanometer :—

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
—	—	17·7	16·0	115–116	146	21·5	**1**	ordinary temperature	constant	total light	acetylene	19
—	—	17·7	16·0	115–116	146	21·5	**21·5**	ditto	constant	total light	acetylene	

<table>
<tr><th>Photographic plate number.</th><th>Electrodes.</th><th>Solution.</th><th>Date of experiment.</th><th>The E.M.F. in the dark, in centimetres on Nalder N1.</th><th>The E.M.F. in the dark, in units of 10^{-6} volts.</th><th>Number of experiment (curve) when the system was exposed to light.</th><th>Maximum constant deflection observed when the system was exposed to light, in milimetres on Nalder N1.</th><th>Resistance of the solution in cell, in ohms.</th><th>Total resistance of circuit, in ohms.</th></tr>
<tr><td>I.</td><td>II.</td><td>III.</td><td>IV.</td><td>V.</td><td>VI.</td><td>VII.</td><td>VIII.</td><td>IX.</td><td>X.</td></tr>
<tr><td colspan="10">TABLE VI.—Ag-BrAg Plates in LiBr, KBr, NaBr Solutions. Influence of the Cation.</td></tr>
<tr><td></td><td>Ag-BrAg in light and in dark</td><td>0·1 normal LiBr</td><td>July 25, 1904</td><td>0·3 centim. to right (200 ohms shunt)</td><td>—</td><td>1, 2</td><td>116, 117</td><td>—</td><td>Resistance of galvanometer = 834·4 ohms, shunt of galvanometer = 1000 ohms</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal KBr</td><td>July 25, 1904</td><td>1·5 centims. to left (1000 ohms shunt)</td><td>—</td><td>3, 4</td><td>120, 117</td><td>—</td><td>ditto</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NaBr</td><td>July 25, 1904</td><td>4·7 centims. to left (1000 ohms shunt)</td><td>—</td><td>5, 6, 7, 8</td><td>136, 112, 114, 114</td><td>—</td><td>ditto</td></tr>
<tr><td colspan="10">The experiments again instituted on February 3 to 7, 1905, with KBr, NaBr, LiBr, NH₄Br solution (with</td></tr>
<tr><td>16</td><td>Ag-BrAg in light and in dark</td><td>0·1 normal KBr</td><td>February 3, 1905</td><td>17 centims. to left</td><td>—</td><td>1, 2</td><td>96·5, 96·5</td><td>12·2</td><td>846·6</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NaBr</td><td>February 3, 1905</td><td>6·1 centims. to left</td><td>—</td><td>3, 4</td><td>85, 86</td><td>17·7</td><td>852·1</td></tr>
<tr><td>17</td><td>ditto</td><td>0·1 normal NaBr</td><td>February 6, 1905</td><td>14 centims. to left</td><td>—</td><td>1, 2, 3</td><td>84, 77, 78</td><td>—</td><td>—</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal LiBr</td><td>February 6, 1905</td><td>13·6 centims. to left</td><td>—</td><td>4, 5, 6</td><td>91, 95, 91</td><td>14·7</td><td>849·1</td></tr>
<tr><td>18</td><td>ditto</td><td>0·1 normal LiBr</td><td>February 7, 1905</td><td>18·5 centims. to left</td><td>—</td><td>1</td><td>92</td><td>—</td><td>—</td></tr>
<tr><td></td><td>ditto</td><td>0·1 normal NH₄Br</td><td>February 7, 1905</td><td>9·5 centims. to left</td><td>—</td><td>2, 3</td><td>98, 98</td><td>11·4</td><td>845·8</td></tr>
<tr><td colspan="10">TABLE VII.—Transformation of the Constant Cell (Ag-BrAg Plates in KBr Solution)</td></tr>
<tr><td>15</td><td>Ag-(BrAg) in light and in dark</td><td>0·1 normal KBr</td><td>November 18, 1904</td><td>8·8 centims. to left (200 ohms shunt)</td><td>—</td><td>1, 2, 3, 4</td><td>73, 60 (corr. 71), 61 (corr. 72), 60 (corr. 75)</td><td>—</td><td>galvanometer shunted with 200 ohms</td></tr>
</table>

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	

(Both sides of each Plate covered with AgBr; Glass Vessel instead of Quartz Vessel used.)

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	Plate
—	—	16·0	16·0	89	123	46·5	12·5	—	constant	total light	acetylene	
—	—	16·0	16·0	89	123	46·5	13·5	—	constant	total light	acetylene	
—	—	16·0	16·0	89	123	47·0	13·5	—	constant	total light	acetylene	

plates cleaned and freshly covered with AgBr on December 17, 1904; one side covered with paraffin):—

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	Plate
—	—	19·2	15·75	115–116	146	20·05	16	—	constant	total light	acetylene	16
—	—	19·2	15·75	115–116	146	20·05	16	—	constant	total light	acetylene	
--	—	19·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	17
--	—	19·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	
--	—	21·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	18
—	—	21·2	16·05	115–116	146	21·5	16	—	constant	total light	acetylene	

into an Inconstant Cell (Ag in Light, KBr Solution, Ag-BrAg in the Dark).

XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	Plate
—	—	16·3	16·2	76	—	58·5	ordinary temperature		inconstant (polarisation)	total light	acetylene	15

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.

TABLE VIII.—Ag-IAg Plates in 0·1 Normal

	Ag-IAg in light and in dark	0·1 normal KI	February 11, 1904	9·5* centims. to right	—	—	—	—	—
	ditto	ditto	February 12, 1904	5·0* centims. to right	—	1, 2, 3	86, 85	15·7	Resistance of galvanometer = 834·4 ohms; shunt of galvanometer = 40 ohms
	ditto	ditto	February 15, 1904	4·5 centims. to right	—	4	35·4	15·7	ditto
	ditto	ditto	February 15, 1904	ditto	—	5	no change	15·7	ditto
	ditto	ditto	February 15, 1904	ditto	—	6	circa 0·5	15·7	ditto
	ditto	ditto	February 17, 1904	5·3* centims. to right	—	(1), 2, 3, 4	112, 118, 123 = average 117·7	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	5	45	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	6	78	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	7	no change	15·7	ditto
	ditto	ditto	February 17, 1904	ditto	—	8	circa 0·5	15·7	ditto
20	ditto	ditto	February 19, 1904	5·0* centims.	—	1	too large to be photographed: over 135	15·7	ditto
	ditto	ditto	February 19, 1904	5·0* centims.	—	2, 3	96, 95	15·7	Resistance of galvanometer = 834·4 ohms; shunt of galvanometer = 20 ohms
	ditto	ditto	February 23, 1904	2·2* centims. to right	—	1, 2	95, 94	15·7	ditto

TABLE IX.—Ag Plates in Decinormal NaBr Solution

24	Ag plates in light and in dark	0·1 normal NaBr and solid AgBr	July 16, 1903	2·9 centims. to right	—	1, 2	64·5, 67·2	—	—
	ditto	ditto	July 16, 1903	ditto	—	3 and 4	25·5 and 72	—	—
	ditto	ditto	July 16, 1903	ditto	—	5 and 6	circa 1 and 9	—	—
	ditto	ditto	July 16, 1903	ditto	—	7 and 8	? and ?	—	—
	ditto	ditto	July 16, 1903	ditto	—	9, 10	12·5, 12·5	—	—
	ditto	ditto	July 16, 1903	ditto	—	11, 12	7·5, 7·5	—	—

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* With shunt of

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given by Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
IK Solution (no Solid IAg added).												
—	—	—	—	—	—	—	—	—	—	—		
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	red screen	arc : 66 volts, 6·2 ampères	
—	—	18·4	16·4	125	—	118	ordinary temperature		constant	green-yellow screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	{ 125	—	118	ordinary temperature		constant	{ blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	red screen	arc : 66 volts, 6·2 ampères	
—	—	18·2	16·8	92	—	118	ordinary temperature		constant	yellow-green screen	arc : 66 volts, 6·2 ampères	
—	—	18·0	16·8	{ 125	—	118	ordinary temperature		constant	{ total light	arc : 66 volts, 6·2 ampères	20
—	—	18·0	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
—	—	18·0	16·8	125	—	118	ordinary temperature		constant	total light	arc : 66 volts, 6·2 ampères	
and Solid AgBr. *Rôle* of the Electrode.												
—		17·3	16·8	82	—	98	—	—	inconstant	total light	arc : 66 volts, 6·2 ampères	24
—	—	17·3	16·8	30 and 42	—	98	—	—	inconstant	blue screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	82 and 30	—	98	—	—	inconstant	red screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	82 and 30	—	98	—	—	inconstant	yellow-green screen	arc : 66 volts, 6·2 ampères	
—	—	17·3	16·8	32	—	59	ordinary temperature		inconstant	total light	acetylene	
—	—	17·3	16·8	42	—	59	ordinary temperature		inconstant	total light	acetylene	

galvanometer = 40 ohms.

Photographic plate number.	Electrodes.	Solution.	Date of experiment.	The E.M.F. in the dark, in centimetres on Nalder N1.	The E.M.F. in the dark, in units of 10^{-6} volts.	Number of experiment (curve) when the system was exposed to light.	Maximum constant deflection observed when the system was exposed to light, in millimetres on Nalder N1.	Resistance of the solution in cell, in ohms.	Total resistance of circuit, in ohms.
I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.

TABLE X.—The Electrical Potential between the

Hg, solid Hg_2Cl_2 in Decinormal NaCl and HCl Solutions,

22	Hg, Hg_2Cl_2 in light and in dark	0·1 normal NaCl	July 25, 1904	10·0 centims.* to left	—		no deflection, perhaps ½	83	Resistance of galvanometer =834·4 ohms; shunt of galvanometer =1000 ohms
	ditto	ditto	July 26, 1904	4·3 centims.* to left	—		no deflection, perhaps ½	83	ditto
	ditto	0·1 normal HCl	July 26, 1904	7·2 centims.* to right	—		no deflection, perhaps ½	83	ditto
	ditto	ditto	July 27, 1904	23·3 centims.* to right	—		no deflection, perhaps ½	83	ditto
21	Hg, Hg_2Br_2 in light and in dark	0·1 normal KBr	February 27, 1904	compensated by opposite E.M.F. 1 centim. to left	—	1 and 2	no deflection	—	no shunt
	ditto	0·1 normal NaBr	February 27, 1904	ditto	—	3	perhaps ½ to 1	—	no shunt

TABLE XI.—Hg, solid Hg_2I_2 in KI Solution, and

Hg, solid Hg_2I_2 in Solution of KI could not be investigated,

23	$Hg_1SO_4Hg_2$ in light and in dark	0·1 normal $SO_4(NH_4)_2$	December 9, 1904	17·8 centims. to left	—	1, 2, 3	44·5, 51·5, 42·5†	—	—
	ditto	ditto	December 9, 1904	ditto	—	4, 5	21, 20·5	—	—

To all the above investigations the intensity of light measured with the Rubens thermopile (Column XVII.) gives the Column XVI., and when the sensitiveness of Nalder No. 2 was that given by

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* With 1000 ohms

† Did not return to zero deflection 12, 6, 5½ millims.; no shunt used with the galvanometer. Height of Hg = circa

Average ampères observed in 10^{-9} units.	Average volts observed in 10^{-6} units.	Calibration of Nalder N1, in centimetres (right and left).	Calibration of Nalder N2, in centimetres (right and left).	Distance of light from quartz vessel, in centimetres.	Distance of light from Rubens thermopile, in centimetres.	Intensity of light measured with Rubens thermopile at the distance given to Column XVI., in millimetres (right and left).	Temperature of bath, in ° C.	Temperature of room, in ° C.	Kind of cell.	Kind of light used.	Volts and ampères when arc was used.	Photographic plate number.
XI.	XII.	XIII.	XIV.	XV.	XVI.	XVII.	XVIII.	XIX.	XX.	XXI.	XXII.	
Illuminated and not Illuminated parts of the Solution.												
Hg, solid Hg_2Br_2 in Decinormal NaBr and KBr Solutions.												
—	—	16·0	16·0	88	123	46, 7	18·7	ordinary temperature	—	total light	acetylene	22
—	—	16·0	16·0	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·2	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·2	88	123	46, 7	18·7	ditto	—	total light	acetylene	
—	—	16·0	16·8	118 and 47	—	98	ordinary temperature		—	total light	arc	21
—	—	16·0	16·8	47	—	98	ordinary temperature		—	total light	arc	
Hg, solid SO_4Hg_2 in Soluble Sulphates, $SO_4(NH_4)_2$, &c.												
since Hg_2I_2 is Decomposed by KI already in the Dark.												
—	—	16·0	16·85	30	98	98	ordinary temperature		constant	total light	arc: 65 volts, 6·1 ampères	23
—	—	16·0	16·85	30	98	98	ordinary temperature		constant	red screen	arc: 65 volts, 6·1 ampères	

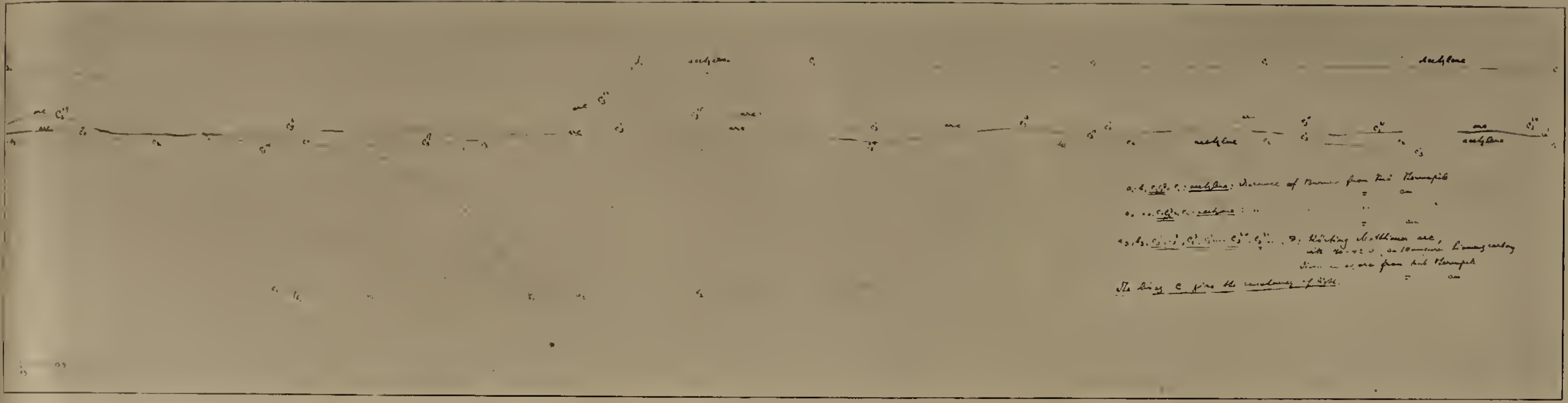
deflections obtained with Nalder N2, when the light was removed from Rubens thermopile, by the distance given in Column XIV. (with a Clark, 100,000 ohms. inserted, and shunt of galv. = 10 ohms.).

---

shunt of galvanometer.

1 centim. Different heights of mercury give different values. The E.M.F. is principally a thermo E.M.F.

7 SEP. [illegible]



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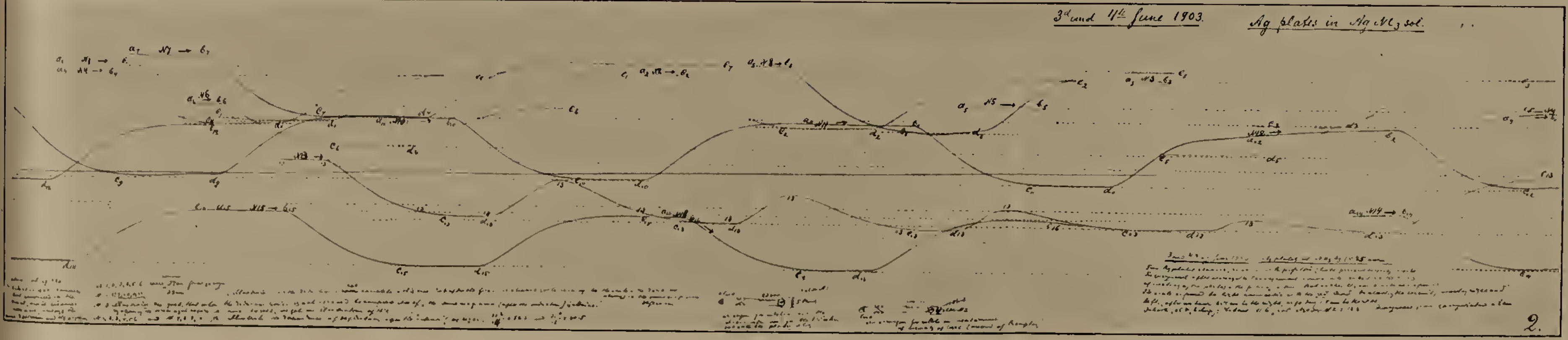

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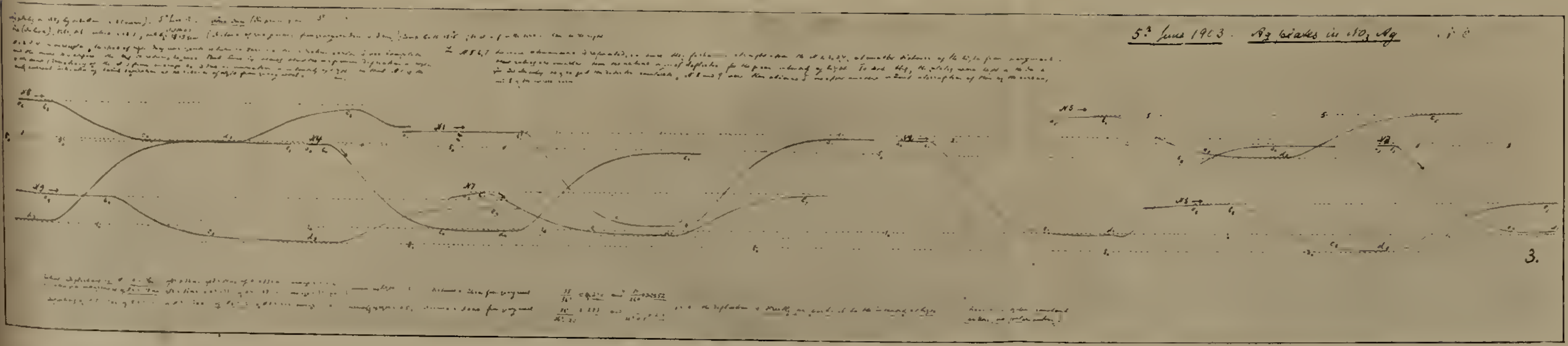

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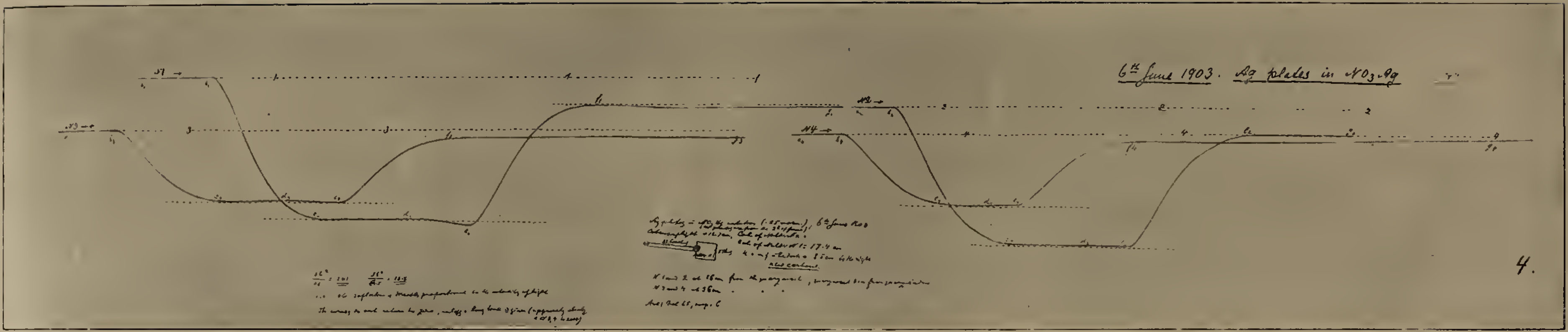

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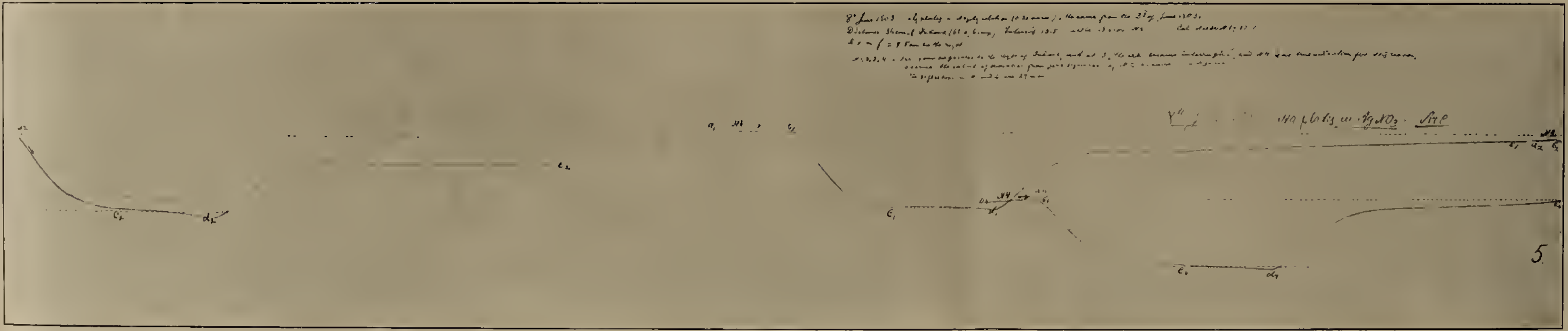

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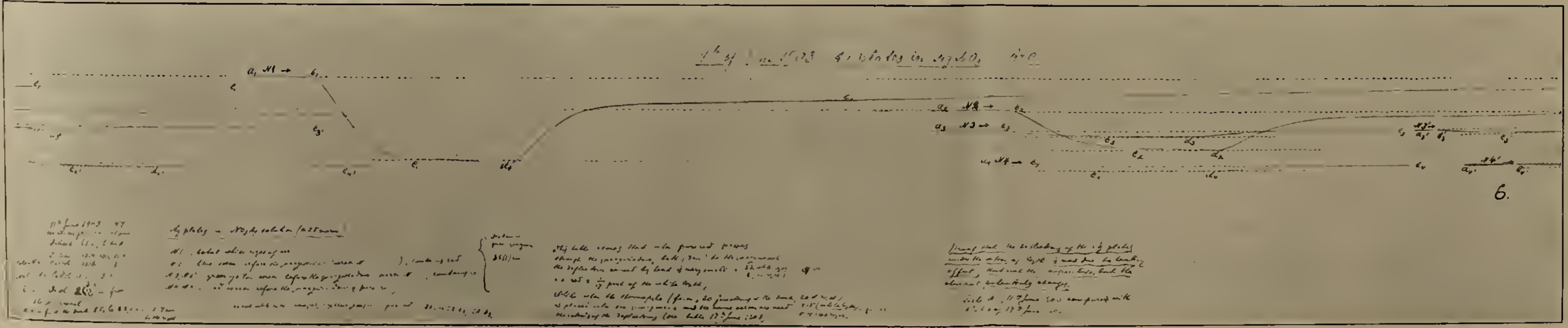

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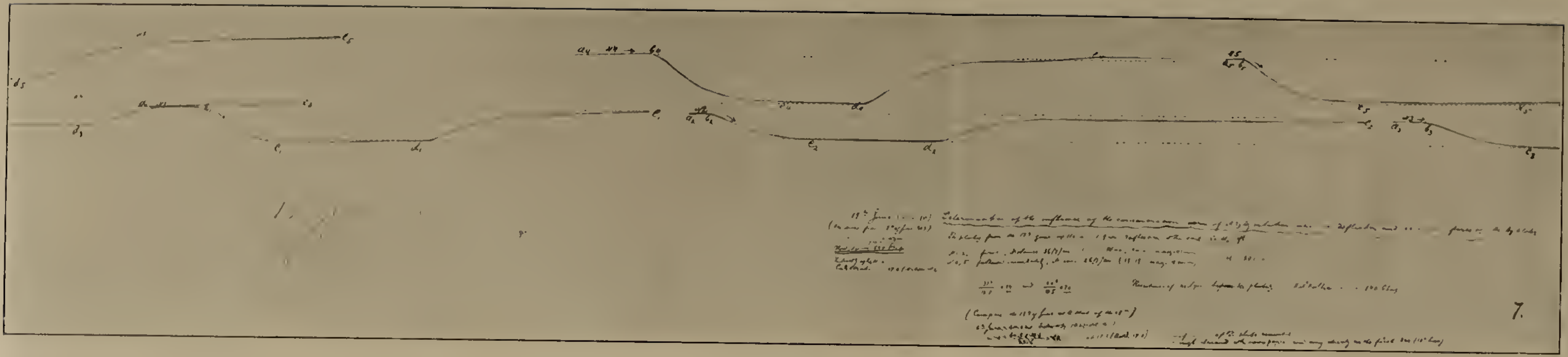

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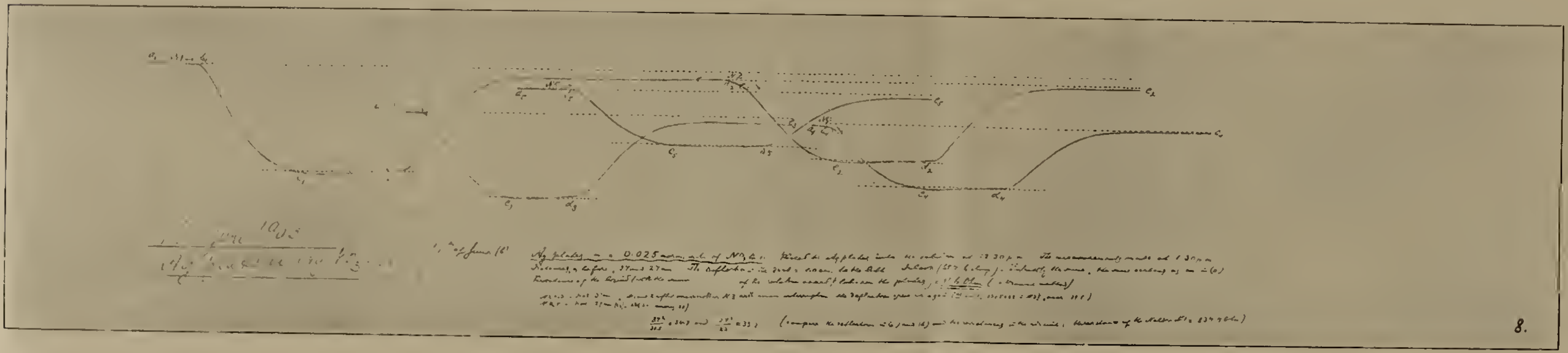

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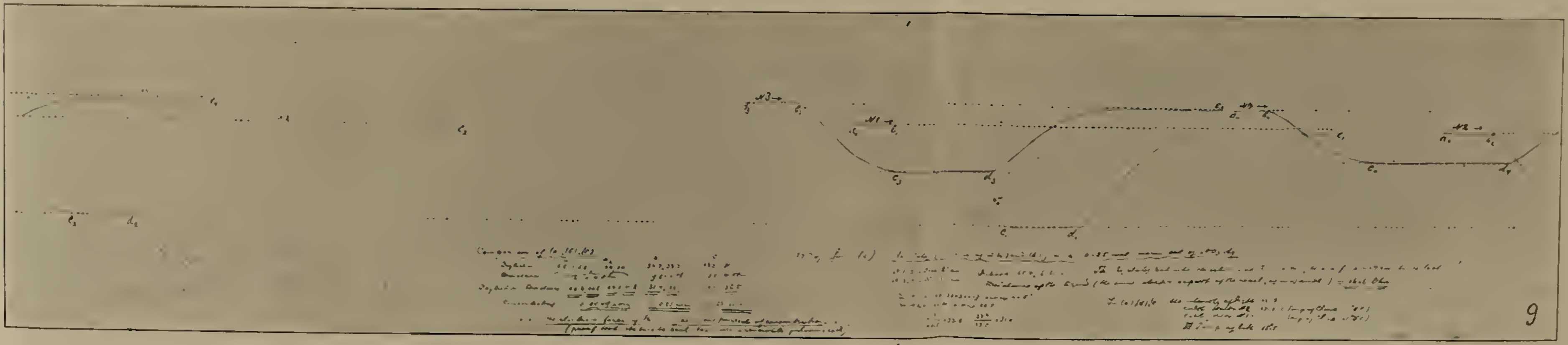

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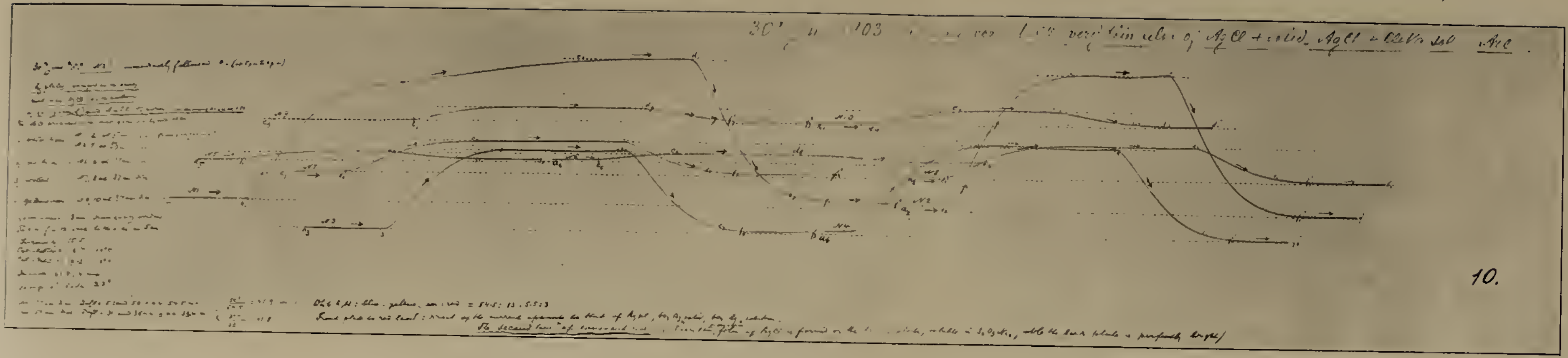

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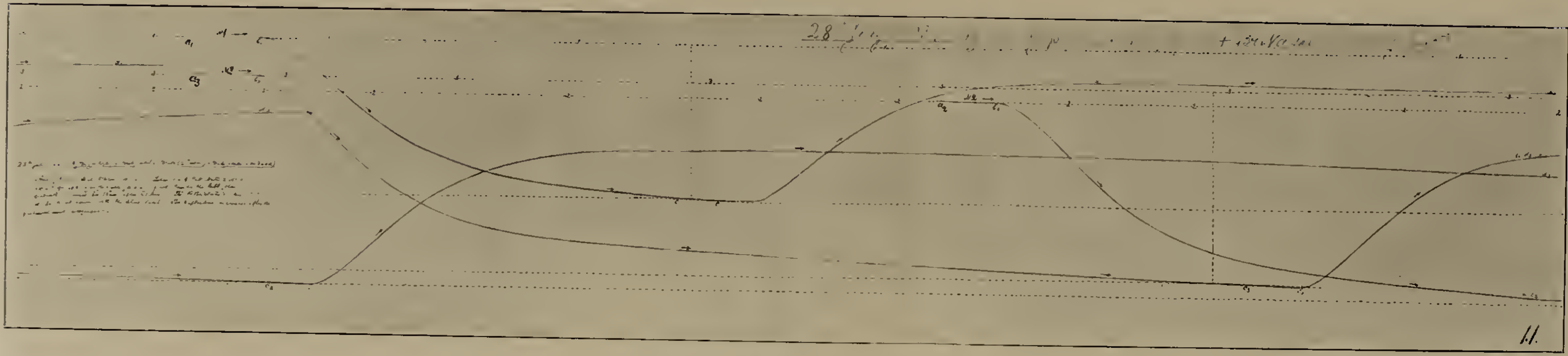

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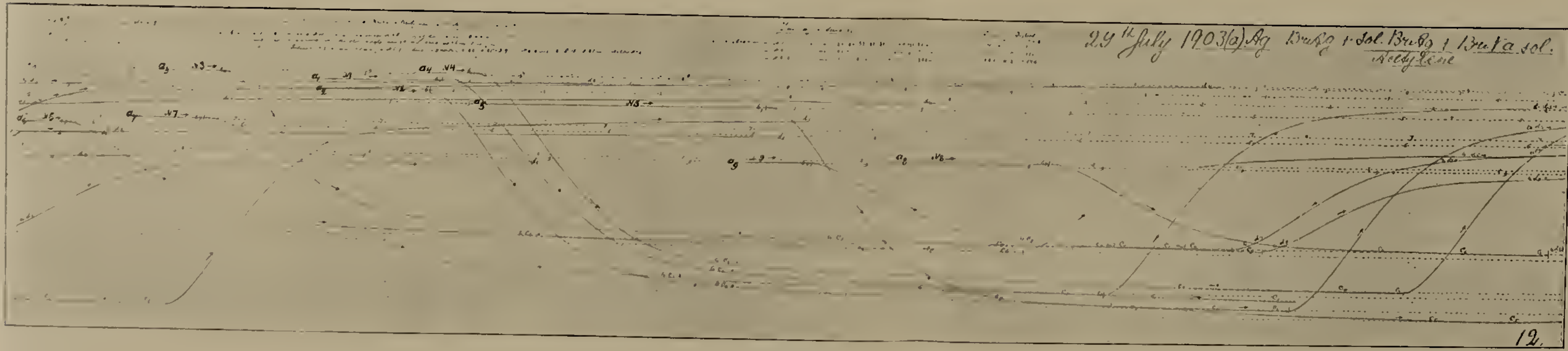

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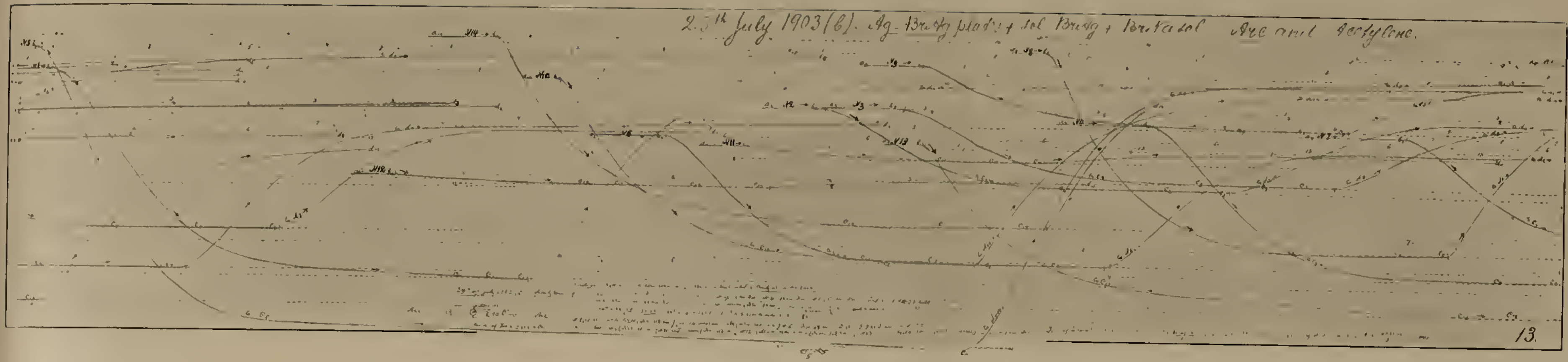

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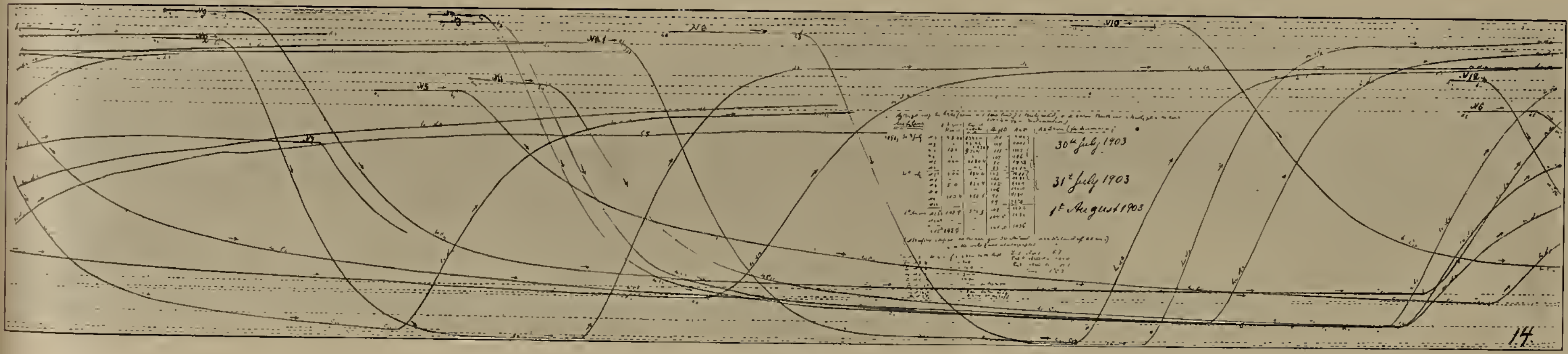

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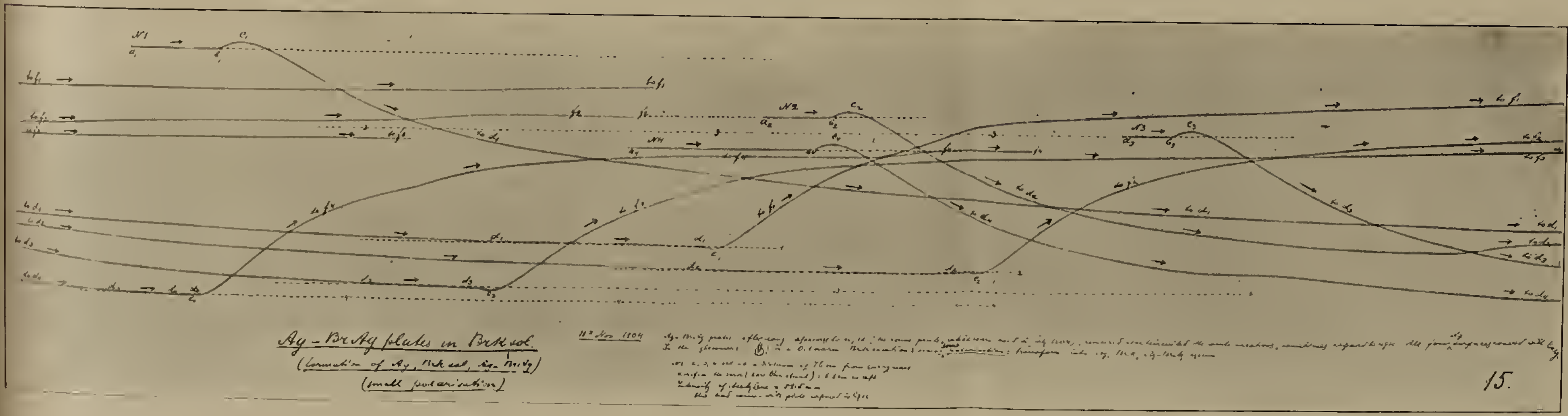

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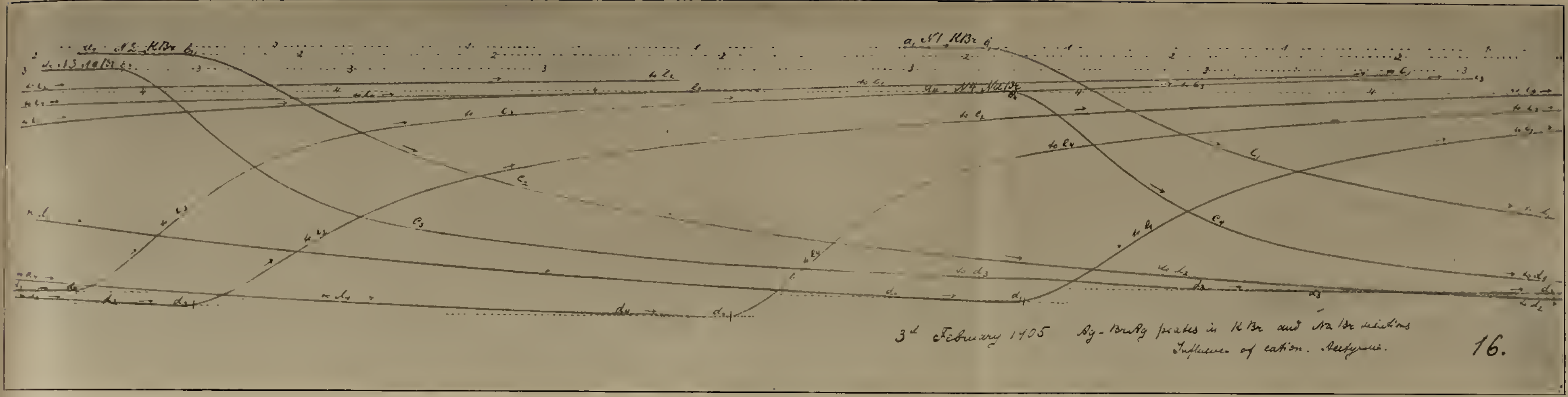

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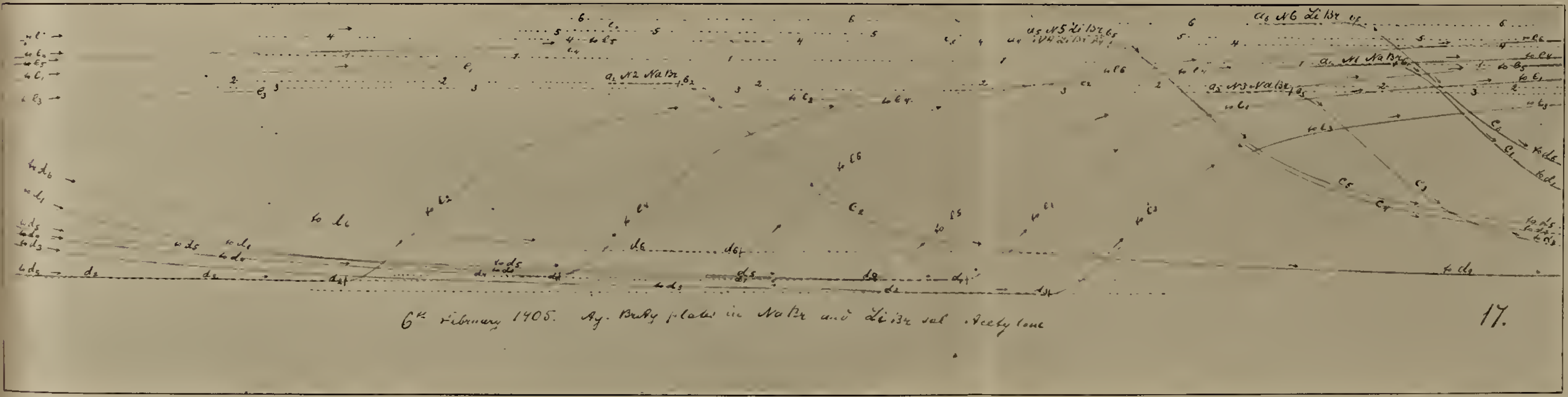

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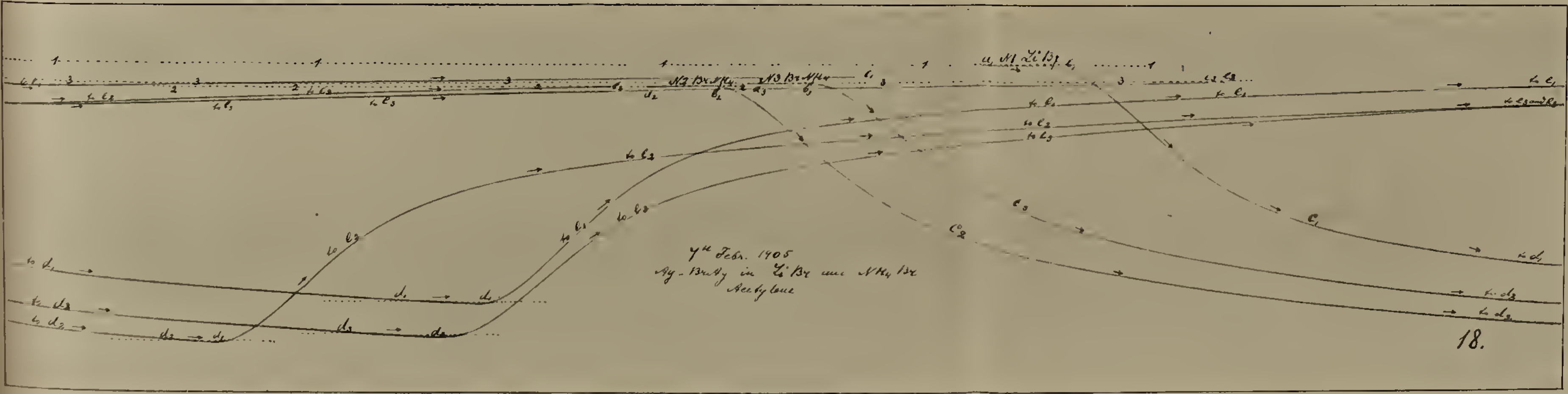

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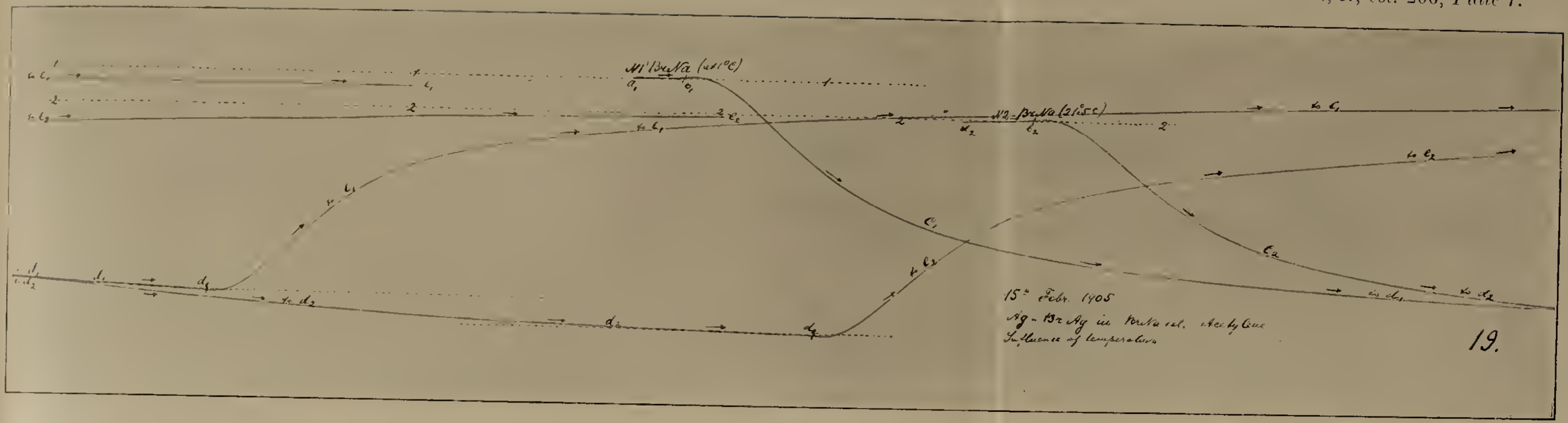

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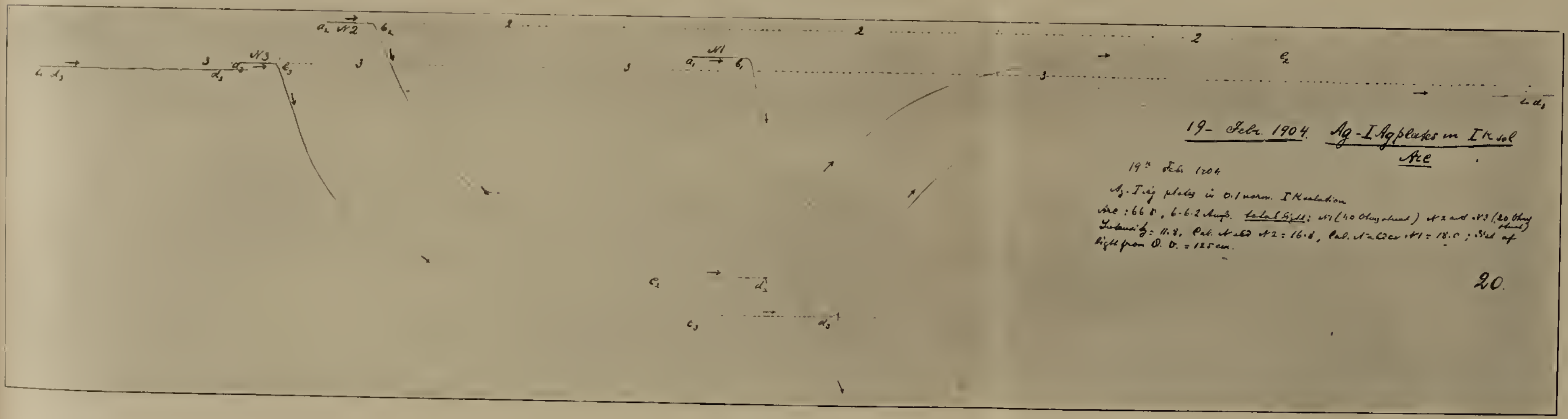

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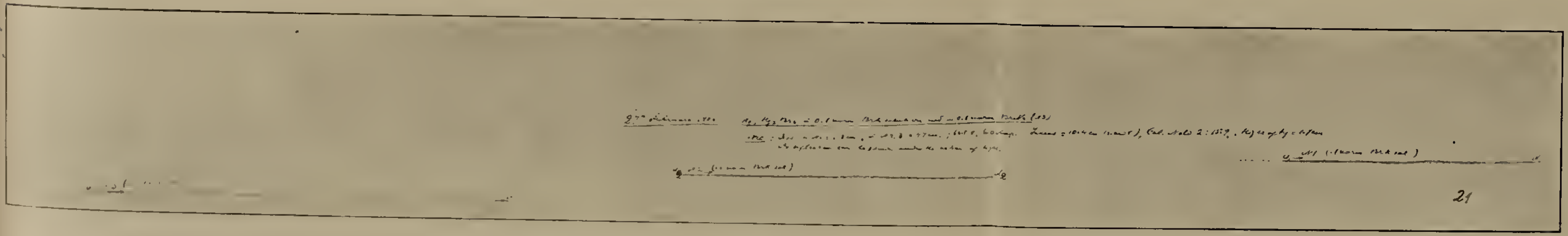

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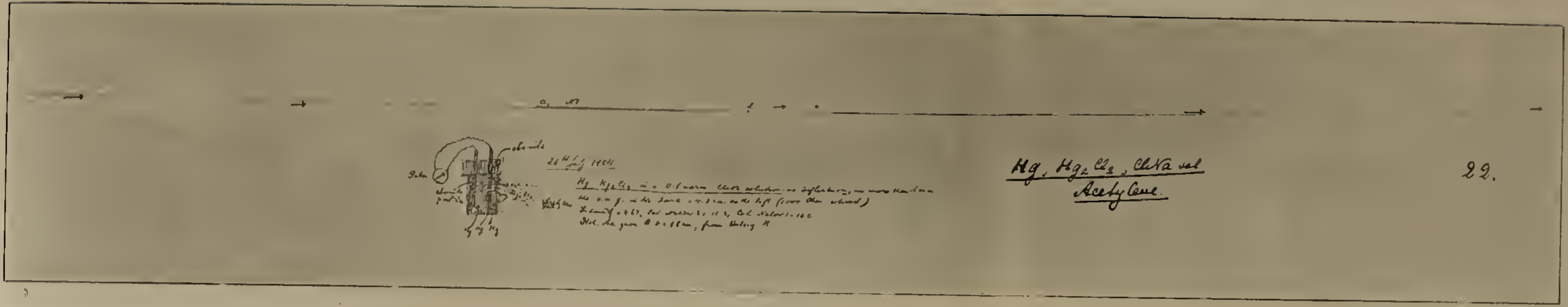

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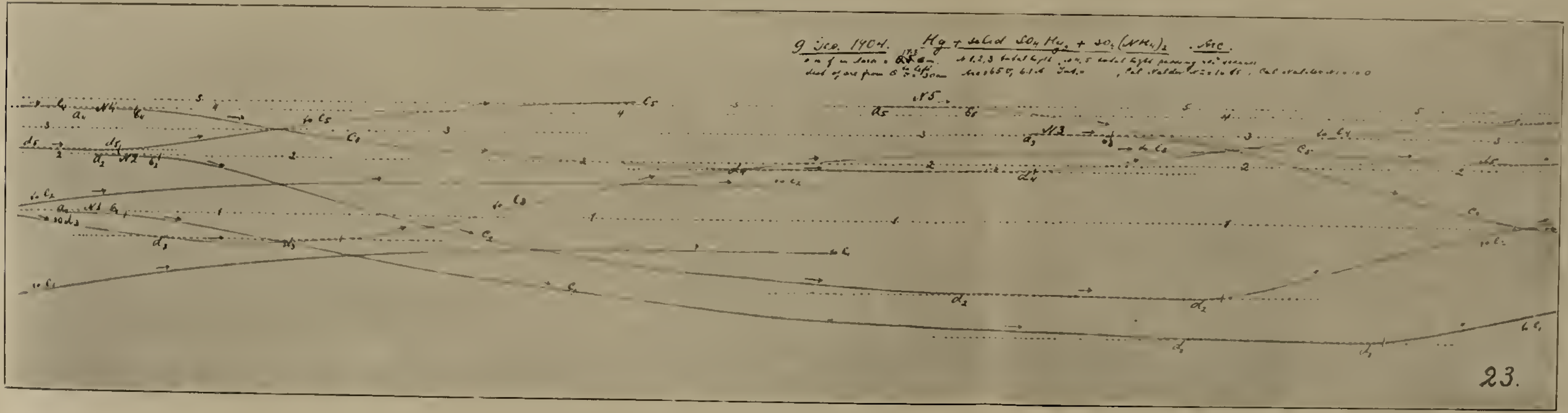

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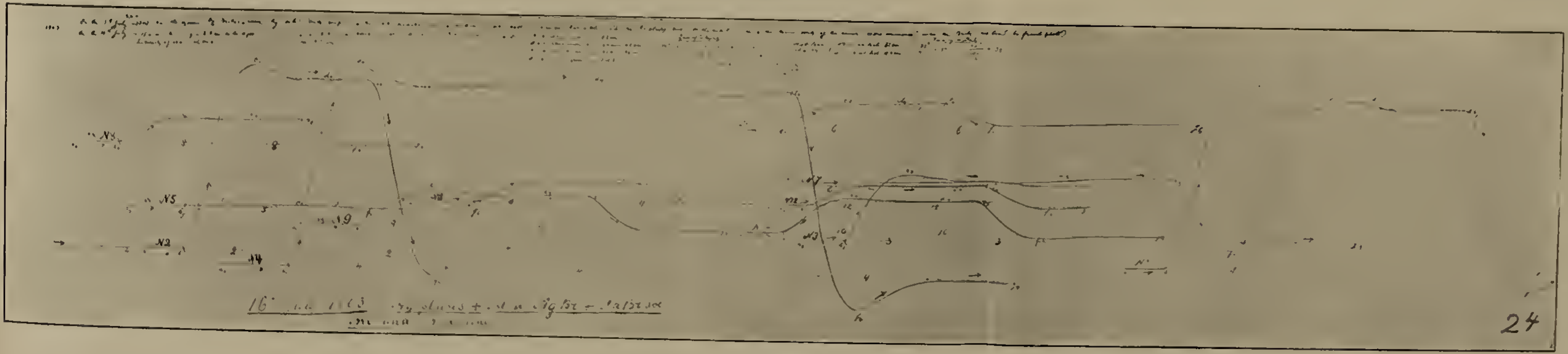

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[PLATE 9.]

DETERMINATIONS OF WAVE-LENGTH FROM SPECTRA OBTAINED AT THE TOTAL SOLAR ECLIPSES OF 1900, 1901 AND 1905

BY

F. W. DYSON, M.A., F.R.S.,
ASTRONOMER ROYAL FOR SCOTLAND, PROFESSOR OF ASTRONOMY IN THE UNIVERSITY OF EDINBURGH
(MEMBER OF THE EXPEDITIONS FROM THE ROYAL OBSERVATORY, GREENWICH).

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VIII. *Determinations of Wave-length from Spectra Obtained at the Total Solar Eclipses of* 1900, 1901 *and* 1905.

By Professor F. W. DYSON, *M.A., F.R.S., Astronomer Royal for Scotland, Professor of Astronomy in the University of Edinburgh. (Member of the Expeditions from the Royal Observatory, Greenwich.)*

Received April 25,—Read May 17, 1906.

[PLATE 9.]

THE following paper consists of a discussion of the photographs of the spectra of the chromosphere and corona obtained in three eclipse expeditions from the Royal Observatory, Greenwich. Preliminary reports of the expeditions of 1900 and 1905, where I was one of Sir WILLIAM CHRISTIE's party, are given in the 'Proceedings,' vol. 67, p. 393, and A, vol. 77, p. 28, and a preliminary report of the expedition to Sumatra in 1901 is given by me in the 'Proceedings,' vol. 69, p. 235. For these eclipse expeditions two spectroscopes were kindly lent by Major HILLS, the same spectroscopes he used for photographing the chromosphere and corona at the Indian eclipse of 1898. Reference is made in the preliminary reports to the large amount of assistance received by voluntary helpers in these expeditions; for special assistance in the spectrographic observations I am greatly indebted to Mr. J. J. ATKINSON, Mr. ARTHUR BERRY, and Captain BRETT. The spectrograms were measured at the Royal Observatory, Greenwich, by Mr. DAVIDSON and myself, and I have profited by Mr. DAVIDSON's assistance and advice in the preliminary arrangement and adjustments of the spectroscopes as well as in the subsequent measurements and discussion.

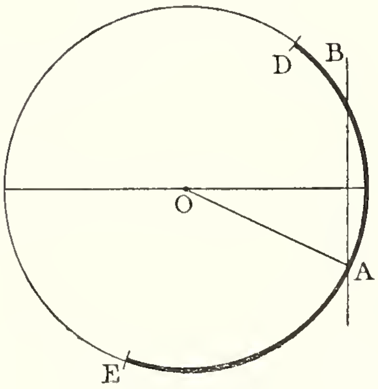
1. Details of the observations and of the adjustments of the spectroscopes are given in the 'Proceedings,' vols. 67, 69, and 77. The following is a brief account of the spectrograms of the chromosphere measured :—

Taken at Ovar, 1900, *May* 28. *Second Contact. Slit a few minutes inside the Tangent to Limb.*

Flint Glass Spectroscope.—Minimum deviation at H_γ.

(No. 6.) Spectrum consists entirely of bright lines and extends from H_β (4862) to K (3933). Only 50 of the brightest lines are shown.

(No. 5.) Spectrum shows between 250 and 300 bright lines, but shows also continuous spectrum and some absorption lines. The definition is good from 4580 to 4100.



(No. 2.) About 150 lines are very strongly shown on the violet side of H_γ. They are short lines standing out from a perfectly black continuous spectrum. If in the diagram A be the point of second contact, and DE be the crescent a little before totality, the image of the sun was adjusted so that the slit might pass through A. Spectrum No. 2 is the spectrum at B, while (5) and (6) are at A.

Quartz Spectroscope.—Minimum deviation at 3650. Quartz objective focussed for 3750.

(No. 8.) Taken after totality and contains 17 lines from h (4101) to Ti (3685). Measured for the wave-lengths of the hydrogen series.

(No. 7.) Taken after totality. Contains 36 lines extending from h (4101) to Ti at 3685.

(No. 6.) Extends from h (4101) to Sc at 3572. This photograph contains 300 lines in excellent definition and free from any continuous spectrum.

(No. 5.) This photograph shows a continuous spectrum with very few absorption lines and 500 bright lines extending from 4180 to 3460.

(No. 4.) Contains about 300 lines between 4170 and 3474. The brightest lines run through the whole spectrum, but, generally speaking, it consists of a continuous spectrum alongside a solar spectrum.

(No. 3.) Contains about 150 lines extending from 4101 to 3510, and approximates in character somewhat to (No. 2).

(No. 2.) Contains about 150 lines from 4101 to 3460 by the side of a solar spectrum, which is over exposed at the blue end, but not in the extreme ultra-violet.

(No. 1.) Shows a few of the strong chromospheric lines in the extreme ultra-violet, between 3510 and 3341. The photograph has been measured and wave-lengths deduced, but as this part of the spectrum was obtained better in Sumatra, the deduced wave-lengths have not been used.

Ovar, 1900, *May* 28. *Third Contact.*

Flint Spectroscope.

(No. 52.) This photograph contains about 300 lines, extending from 4670 to 4026. There is a continuous spectrum with a very occasional absorption line. There are a few lines to the red of 4670 and the violet of 4026, but the definition is not good and they have not been measured.

Quartz Spectroscope.

(No. 14.) Contains 20 lines from 4101 to 3685.

(No. 15.) Contains 100 lines from 4179 to 3613. No continuous spectrum.

(No. 16.) Contains 160 lines from 4179 to 3572. Beyond this point the definition is bad and the spectrum not used. The lines are seen on a continuous spectrum in which practically no absorption lines are seen.

(No. 17.) Contains about 130 lines and extends from 4101 to 3474. The chromospheric lines are short tips by the side of a continuous spectrum which shows absorption lines at the violet end, but is much over-exposed in the blue.

The programme of observations in 1901 was arranged to supplement as far as possible those made in 1900 with the flint glass spectroscope towards the red and with the quartz spectroscope in the ultra-violet. A suggestion of Mr. DAVIDSON's was used to give a longer piece of spectrum in focus, two plates inclined at a suitable angle being used instead of one.

1901, *May* 17, *Sumatra.*

Flint Spectroscope.—Minimum deviation H_γ.

(No. 5.) Contains 200 lines from 5670 to 4426 and 70 lines from 4401 to 4077. This photograph consists entirely of bright lines with no continuous spectrum.

(No. 4.) Contains 180 lines from 5658 to 4460 and 60 lines from 4401 to 4101. The spectrum is measured on the edge of a continuous spectrum.

Quartz Spectroscope.—Minimum deviation 3400. Objective focussed for 3400.

(No. 7.) Contains 20 lines from 3970 to 3685 with no continuous spectrum.

(No. 6.) Contains 160 lines from 4036 to 3641 with no continuous spectrum.

(No. 5.) Contains 160 lines from 4042 to 3600. The chromospheric spectrum is measured on the two edges of the continuous spectrum.

(No. 3.) About 100 lines are measured on the sides of the continuous spectrum from 4035 to 3510. At about this point the band divides into two parts, the continuous spectrum disappears, and the chromospheric spectrum is seen as two series of dots or very short lines. About 100 lines are shown between these limits. The explanation of this spectrum is that the crescent was cut by the slit in two points, each of which furnishes a chromospheric spectrum; these spectra are quite clear and distinct from 3500 to 3300 (the quartz objective being focussed for wave-length 3400), but nearer the blue end of the spectrum the want of focus of the objective introduces the solar spectrum as well.

The measurement of the spectra in which there was no continuous spectrum presented no difficulties, and, generally speaking, where there was a continuous spectrum the bright lines were sufficiently strong across it and showed tips at the edges to make their identification and measurement quite certain. In cases where the absorption lines in the solar spectrum are very strong, the corresponding chromospheric lines were to some extent weakened and uncertain in parts of the spectrum for which the objective was not in focus. Some of these lines, *e.g.*, 4063·76 Fe 20 (in ⊙), 4071·91 Fe 15 (in ⊙), are not shown as strongly as in Sir NORMAN LOCKYER's and other spectra, where an objective prism was used.

2. The spectra were measured by comparison with a glass scale whose division errors had been previously determined. Wave-lengths were determined from each photograph, in some cases by interpolation from a table and in others by HARTMANN's formula. It seemed impracticable to give all the results from the separate photographs, and the means only are given. The number of photographs on which a line has been measured is given as well as the intensity. The scale of intensities must be considered as applying to lines in neighbouring parts of the spectrum.

The following table, extending from the titanium line at 3685 to the end of the series of hydrogen lines, is given as a specimen of the results of the separate photographs. The numbers at the head of the columns refer to the separate photographs taken with the quartz spectroscope :—

Wave-length.											Intensity.											Deduced wave-length and intensity.	
Sumatra.			Ovar.								Sumatra.			Ovar.									
			Second contact.					Third contact.						Second contact.					Third contact.				
5.	3.	6.	2.	3.	4.	5.	6.	15.	16.	17.	5.	3.	6.	2.	3.	4.	5.	6.	15.	16.	17.		
—	—	—	·80	·97	·88	·88	·88	—	·93	·84	—	—	—	1	1	3	2	2	—	1	1	3659·88	2
—	—	—	—	—	—	·73	—	—	—	—	—	—	—	—	—	—	0	—	—	—	—	3660·73	0
—	—	—	—	·28	—	·44	·46	—	—	—	—	1	—	—	—	—	0	0	—	—	—	3661·39	1
—	·24	—	·36	·36	·35	·35	·40	—	·37	·37	—	1	—	3	1	3	3	2	—	2	2	3662·35	3
—	—	—	—	—	—	·11	—	—	·99	—	—	—	—	—	—	—	1	—	—	0	—	3663·05	1
—	·49	—	—	·51	·59	·51	·62	—	·72	·60	—	1	—	—	0	2	1	0	—	1	1	3663·58	2
—	·86	—	·73	·78	·75	·73	·82	—	·75	·81	—	1	—	2	1	3	2	1	—	1	1	3664·78	3
—	—	—	—	—	—	·33	—	—	—	—	—	—	—	—	—	—	0	—	—	—	—	3665·33	0
—	·31	—	·22	·16	·13	·18	·15	—	·30	—	—	1	—	2	1	1	2	1	—	1	—	3666·21	2
—	—	—	—	—	—	·23	·26	—	—	—	—	—	—	—	—	—	1	1	—	—	—	3667·25	1
—	·99	—	·84	·81	·89	·90	·89	—	·96	·85	—	1	—	2	1	1	1	1	—	1	1	3667·89	2
—	—	—	—	—	—	·61	—	—	—	—	—	—	—	—	—	—	0	—	—	—	—	3668·61	0
·47	·51	—	·50	·61	·58	·54	·60	—	·67	·70	1	0	—	2	2	2	2	2	—	1	1	3669·58	2
—	—	—	—	—	—	·62	—	—	—	—	—	—	—	—	—	—	1	—	—	—	—	3670·62	1
·34	·42	—	·43	·41	·50	·51	·58	—	·48	·50	1	1	—	2	1	3	2	2	—	2	2	3671·46	3
—	—	—	—	·75	—	·71	—	—	—	—	—	—	—	—	1	—	0	—	—	—	—	3671·73	0
—	—	—	—	—	·37	·48	—	—	·45	—	—	—	—	—	—	1	1	—	—	0	—	3672·43	1
—	—	—	—	—	—	—	·81	—	—	—	—	—	—	—	—	—	—	0	—	—	—	3672·81	0
·83	·91	—	—	·92	·92	·87	·95	—	·85	·97	1	1	—	—	2	2	2	2	—	1	2	3673·90	2
—	·75	—	·82	·80	·85	·85	·93	—	·85	·96	—	1	—	1	1	2	2	1	—	0	2	3674·85	2
—	—	—	—	—	—	·87	—	—	—	—	—	—	—	—	—	—	0	—	—	—	—	3675·87	0
·45	·51	·54	·50	·53	·56	·57	·52	·57	·62	·51	2	2	1	2	2	3	2	3	0	2	2	3676·54	3
—	—	—	·69	—	—	—	—	—	·58	—	—	—	—	1	—	—	—	—	—	0	—	3677·64	1
·01	·82	·82	·93	·89	·87	·91	·89	·97	·99	·99	0	1	1	1	1	3	2	3	0	1	2	3677·92	3
·46	·57	·54	·45	·48	·48	·47	·46	·53	·53	·52	1	2	1	2	2	3	2	3	0	1	2	3679·50	3
—	—	—	·95	·08	—	·99	·02	—	—	—	—	—	—	1	1	—	1	1	—	—	—	3680·01	1
—	—	—	·95	—	·00	·00	—	—	·09	—	—	—	—	1	—	1	1	—	—	0	—	3681·01	1
—	—	—	—	—	—	·50	—	—	—	—	—	—	—	—	—	—	1	—	—	—	—	3681·50	0
—	—	—	—	—	·38	·35	—	—	—	—	—	—	—	—	—	0	1	—	—	—	—	3682·37	1
·87	·75	·88	·02	·92	·96	·94	·98	·94	·89	·97	1	3	1	2	3	3	3	4	1	2	2	3682·92	4
—	—	—	—	—	·68	·67	·74	—	—	—	—	—	—	—	—	0	0	0	—	—	—	3683·70	0
—	—	—	·30	—	·37	·29	·35	—	·36	·37	—	—	—	1	—	3	1	2	—	0	1	3684·34	2
·36	·38	·33	·41	·34	·34	·34	·31	·33	·38	·41	8	9	7	6	6	10	10	15	10	10	6	3685·35	15

As regards the identification of the lines, Rowland's Solar Spectrum was first compared with the chromospheric spectrum, and was, to a certain extent, a very good guide. Comparison with arc spectra—*e.g.*, the titanium, chromium, &c., spectra of Hasselberg—was generally speaking a complete failure. Comparison was next made with Exner and Haschek's Spark Spectra, and the great majority of the stronger lines of the chromospheric spectrum were at once seen to be strong spark-lines of titanium, chromium, scandium, yttrium, iron, manganese, and zirconium.

It seemed desirable to give with the wave-lengths the intensities in the sun and in the spark, and for completeness the intensity in the arc is also given. The intensities in the sun were taken from Rowland, in the spark from Exner and Haschek, in the arc from Kayser and Runge for iron, Ca, Mg, Al, &c.; from Hasselberg for titanium, chromium, manganese, nickel and cobalt; from Rowland and Tatnall for zirconium, vanadium and lanthanum. The intensities in the arc spectra were revised and many additions to the intensities both in the arc and spark were afterwards made from Mr. Jewell's discussion of his observations at Pinehurst (Publications of U.S. Naval Observatory, Washington, 1905). In the column giving the intensity in the arc, 0 denotes that the line is not found in the list with which comparison has been made to distinguish from —, where no information has been found. I have not attempted to push the identification of the lines further than seemed reasonably probable.

For the part of the spectrum from H_β to D_3, which depends entirely on photographs taken in Sumatra, I have given Mr. Lord's results for comparison. The definition of my spectra in this part was not very good.

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Intensity.			Spark.	Arc.	Sun.	
3295·91	1	2	—	—	—	—	—	
3302·98	1	2	—	—	—	—	—	Probably Na.
3303·48	1	1	—	—	—	—	—	
3313·92	1	0	—	—	—	—	—	
3321·54	1	1	—	—	—	—	—	
3323·00	2	2	Ti	3323·06	30	—	5	
3324·14	1	0	—	3324·20	—	—	4N	
3326·87	1	1	Ti	3326·91	10	—	5	
3329·53	2	2	Ti	3329·57	20	—	5	
3332·18	2	1	Ti	3332·24	15	—	3	
3335·29	2	2	Ti	3335·30	20	—	4	
3336·51	1	1	Cr	3336·48	8	—		
3339·99	1	1	Cr	3339·99	10	—	3	
3340·48	2	3	Ti	3340·46	15	—	3	
3341·98	2	4	Ti	3341·97	20	—	4	
3342·72	1	1	Cr	3342·72	10	—	3	
3343·90	1	0	Ti	3343·91	7	3	4	
3346·95	1	1	Ti	3346·90	7	8	2	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3347·98	1	1	Cr	3347·97	6	—	3	
3349·14	2	5	Ti	3349·17	20	3	9	
3349·55	2	5	Ti	3349·60	10	—	7	
3349·81	1	0	—	—	—	—	—	
3353·84	1	1	Sc	3353·88	20	—	4	
3358·65	1	2	Cr	3358·65	9	—	4	Identified in sun as Ti, Cr.
3360·36	1	2	Cr	3360·48	10	3	1	
3361·34	2	6	Ti	3361·33	50	10	8	
3368·20	2	5	Cr	3368·19	10	5	5	
3369·04	1	1	Sc	3369·08	10	—	3	
3372·37	2	1	Sc Ti	3372·31 3372·36	10 4	— —	0 2	
3372·95	2	10	Ti	3372·95	30	10	10	Identified in sun as Ti, Pd.
3374·46	1	0	Ti	3374·49	4	—	2	Identified in sun as Ti, Co.
3378·51	2	1	Cr	3378·51	8	—	2	Identified in sun as Cr, Co ?
3379·98	2	1	Cr	3379·96	9	3	3	
3380·49	2	2	Ti	3380·40	15	7	3	
3381·59	1	0	—	—	—	—	—	
3382·85	2	2	Cr	3382·83	9	—	4	Identified in sun as Cr, Mn.
3383·91	2	8	Ti	3383·89	50	10	3	
3387·99	2	5	Ti	3387·99	15	5	—	
3391·56	1	0	Cr	3391·58	8	—	2	
3392·12	2	1	Zr	3392·11	15	10	2	
3392·75	1	0	Fe	3392·76	3	8	2	Identification doubtful.
3393·18	2	1	Cr	3393·16	8	—	1	
3393·95	1	1	Cr	3393·98	8	—	2	
3394·68	2	5	Ti	3394·69	30	5	3	
3399·11	1	0	—	—	—	—	—	3399·3 (EVERSHED).
3402·53	2	2	Ti	3402·55	8	—	3	
3403·48	2	3	Cr	3403·40	10	—	2	
3404·95	1	1	Zr	3404·97	6	5	0	
3406·72	1	0	—	3406·70	—	—	0	
3407·46	1	1	—	3407·45	—	—	2	
3408·92	2	4	Cr	3408·91	10	3	3	
3409·96	1	0	Ti	3409·95	4	—	2	
3410·39	1	2	Zr	3410·39	8	1	1	
3411·52	1	0	—	—	—	—	—	
3412·63	1	0	Co	3412·63	10 10	— —	5 4	
3413·19	1	0	—	—	—	—	—	3413·0 (?) (EVERSHED).
3415·37	1	0	—	—	—	—	—	3415·01 (EVERSHED).
3416·07	1	0	—	—	—	—	—	Very faint and somewhat doubtful.
3417·94	1	0	—	3417·95	—	—	2	
3418·88	1	0	—	—	—	—	—	
3419·57	1	0	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Inten-sity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3420·31	1	1	—	—	—	—	—	
3421·37	2	4	Cr	3421·35	10	3	4	
3422·86	2	4	Cr	3422·89	10	4	4	
3424·87	2	0	—	—	—	—	—	
3425·72	1	0	—	3425·72	—	—	1s	
3428·47	1	0	—	—	—	—	—	
3429·85	1	0	—	—	—	—	—	
3430·71	1	1	Zr	3430·67	10	3	1	
3431·63	1	1	Co	3431·72	10	—	4	
3432·41	1	1	Co	3432·45	4	—	0	? Identification.
3433·42	2	5	Cr	3433·45	10	3	3	
3437·15	2	1	—	—	—	—	—	
3438·38	2	2	Zr	3438·38	15	5	2	
3439·20	1	2	—	—	—	—	—	
3440·04	1	0	—	—	—	—	—	
3440·72	2	1	Fe	3440·76	7	10	20	
3441·20	1	1	Fe	3441·15	6	10	15	
3442·14	2	4	Mn	3442·12	40	7	6	
3443·48	2	1	—	3443·52	—	—	1	
3444·46	2	2	Ti	3444·47	15	5	4	
3452·61	1	1	Ti	3452·61	9	—	1	
3456·14	1	1	—	—	—	—	—	
3458·99	1	1	—	—	—	—	—	
3460·46	4	3	Mn	3460·46	40	5	4	
3461·68	3	2	Ti	3461·63	15	5	5	
3462·42	1	1	—	—	—	—	—	
3463·06	2	1	Co	3462·95	20	—	6	
			Zr	3463·15	12	3	0	
3465·83	1	1	Co	3465·90	20	7	4	
3474·30	5	2	Mn	3474·20	30	0	2	
				3474·29			2	
3475·75	4	0	Fe	3475·59	10	8	10	
3477·32	4	2	Ti	3477·32	15	5	5	
3479·02	1	0	—	—	—	—	—	
3479·48	2	1	Zr	3479·53	10	0	2	
3481·31	3	2	Zr	3481·30	10	5	2	Identified in sun as Pd, Ti-Zr.
3482·99	3	2	Mn	3483·05	30	4	5	
3488·01	2	1	—	—	—	—	—	
3488·84	5	2	Mn	3488·82	30	4	4	
3489·88	2	1	Ti	3489·89	4	3	2	Identified in sun as Ti, Pd.
3491·18	5	2	Ti	3491·20	10	5	5	
3491·99	1	0	—	—	—	—	—	
3492·79	1	0	—	—	—	—	—	
3494·71	5	1	—	—	—	—	—	3494·60 (EVERSHED).
3496·33	5	2	Zr	3496·35	20	7	2	

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Intensity.			Spark.	Arc.	Sun.	
3497·67	4	2	Mn	3497·67	20	3	3	
3499·17	2	1	—	—	—	—	—	3499·14 (Evershed).
3500·45	1	1	Ti	3500·47	5	3	3	
3501·70	1	1	—	—	—	—	—	
3505·02	4	2	Ti	3505·06	50	6	2	
3505·77	3	1	Zr	3505·81	8	4	1	Identified in sun as Zr V.
3507·50	2	1	—	—	—	—	—	
3509·23	1	0	—	—	—	—	—	
3510·50	2	1	Ni	3510·47	10	8	8	
3511·00	5	3	Ti	3510·99	50	5	5	
3511·68	2	0	—	—	—	—	—	
3512·18	1	0	—	—	—	—	—	
3512·65	1	0	—	—	—	—	—	
3514·33	1	1	—	—	—	—	—	
3517·21	1	1	La	(3517·26)	50	0	—	
3517·51	3	1	V	3517·45	10	1	3	
3519·94	1	0	Ni	3519·90	15	3	7	
3520·21	1	0	V	3520·17	7	0	2	
3520·44	2	1	Ti	3520·40	20	4	2	
3524·77	2	1	Ni	3524·68	15	30	20	
3526·04	1	1	Fe Fe	3525·98 3526·18	4 4	— 4	4 6	
3526·75	1	0	—	—	—	—	—	3526·59 (Evershed).
3527·64	1	0	—	—	—	—	—	
3528·68	1	0	—	—	—	—	—	
3530·14	1	1	—	—	—	—	—	
3530·90	4	2	V	3530·92	10	0	3	
3531·85	4	1	—	3531·85	—	—	1	3531·83 (Evershed).
3532·77	1	0	—	—	—	—	—	
3533·81	1	0	—	—	—	—	—	
3535·06	1	1	—	—	—	—	—	
3535·58	3	2	Ti	3535·55	20	4	4	
3535·95	3	1	Sc	3535·87	15	—	3	
3536·68	2	1	Fe	3536·71	6	4	7	
3537·05	1	0	—	—	—	—	—	
3542·58	1	0	—	—	—	—	—	
3543·50	1	0	—	—	—	—	—	
3544·31	3	1	—	3544·37	—	—	1	
3545·27	3	1	V	3545·34	10	1	4	
3546·09	1	0	—	—	—	—	—	
3546·92	1	0	—	—	—	—	—	
3547·79	1	1	—	—	—	—	—	3548·08 (Evershed).
3549·17	4	2	Y	3549·15	20	7	2	
3549·60	2	1	Gd	(3549·53)	10	—	—	? Identification.
3550·41	1	1	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			
					Spark.	Arc.	Sun.	
3551·22	1	0	—	—	—	—	—	
3552·11	3	2	Zr	3552·10	10	3	1	
3553·20	3	2	—	—	—	—	—	3553·5 (EVERSHED).
3553·84	1	1	—	—	—	—	—	
3554·39	1	0	—	—	—	—	—	
3555·28	1	1	—	—	—	—	—	3555·02 (EVERSHED).
3556·81	3	3	Zr	3556·74	15	5	2	
3558·54	1	0	Fe	3558·67	4	9	8	
3563·25	1	0	—	—	—	—	—	
3565·56	3	1	Fe	3565·54	8	10	12	
3566·21	3	1	Ti	3566·11	5	3	1	
			V	3566·31	6	0	2N	
3566·48	1	0	Ni	3566·52	20	9	10	
3567·86	4	1	Sc	3567·84	20	—	4	
3568·34	2	1	—	—	—	—	—	
3569·44	1	0	Co	3569·52	20	10	5	
3570·30	4	1	Fe	3570·27	10	8 8	20	
3571·01	1	0	—	—	—	—	—	
3571·69	1	0	—	—	—	—	—	
3572·10	1	0	Ni	3572·01	10	7	6	
			Fe	3572·16	2	2	5	
3572·68	9	2	Zr	3572·62	12	10	4	Probably Sc.
			Sc	3572·71	50	—	6	
3573·19	1	0	—	—	—	—	—	
3573·52	1	1	—	—	—	—	—	
3573·83	3	1	Ti	3573·79	7	4	2	
3574·88	1	0	—	—	—	—	—	
3575·33	2	0	—	—	—	—	—	
3575·64	1	0	—	—	—	—	—	
3575·95	1	0	—	—	—	—	—	
3576·48	9	4	Sc	3576·53	30	20	7	
3577·00	5	2	Zr	3577·00	10	0	1	
3577·67	2	0	—	—	—	—	—	
3578·23	2	0	—	—	—	—	—	
3578·89	4	1	Cr	3578·83	10	30	10	
3579·35	1	0	—	—	—	—	—	
3581·08	1	1	Sc	3581·07	20	—	5	
3581·29	7	1	Fe	3581·35	10	10	20	
3582·01	1	0	—	—	—	—	—	
3583·81	1	0	—	—	—	—	—	
3584·67	2	1	Y	3584·66	10	6	2	
3584·91	1	0	—	—	—	—	—	
3587·13	2	0	Fe	3587·13	5	8	8	
3587·71	1	1	—	—	—	—	—	3587·61 (EVERSHED).

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Inten-sity.			Spark.	Arc.	Sun.	
3588·33	2	1	—	—	—	—	—	
3588·97	2	1	—	—	—	—	—	
3589·83	6	3	Sc	3589·77	10	—	5	
			V	3589·91	9	1	5d ?	
3590·64	7	3	Sc	3590·63	10	—	4	
3591·51	1	0	—	—	—	—	—	3591·72 (EVERSHED).
3592·16	7	3	V	3592·17	9	1	2	
3592·78	2	1	—	—	—	—	—	
3593·60	6	2	Cr	3593·64	10	30	9	
3595·10	3	1	Co	3595·02	10	7	3	
3596·20	7	2	Ti	3596·20	10	3	4	
3597·91	2	1	Ni	3597·86	10	7	8	
3600·89	9	3	Y	3600·88	50	10	3	
3602·05	8	3	Y	3602·06	20	6	1	
3602·94	1	1	—	—	—	—	—	
3603·32	1	1	—	—	—	—	—	3603·38. Wide line (EVERSHED).
3603·69	1	1	—	—	—	—	—	
3603·90	4	2	Cr	3603·92	9	0	3	
3605·48	4	1	Cr	3605·48	10	20	7	
3606·73	3	1	—	—	—	—	—	3606·83 (EVERSHED).
3607·55	2	0	Zr	(3607·60)	6	0	—	Identification doubtful.
3609·01	4	1	Fe	3609·01	20	8	9	
3609·79	3	2	—	—	—	—	—	
3611·15	7	3	Y	3611·19	30	7	2	
3611·94	4	1	Co –	3611·86	7	5	2	
			Zr	3612·04	10	1	00	
3612·65	3	0	—	—	—	—	—	
3613·27	6	2	Cr	(3613·35)	6	0	—	
3613·98	10	4	Sc	3613·95	100	4	4	
3614·88	7	3	Zr	3614·92	10	5	2	
3615·68	1	1	—	—	—	—	—	
3616·83	1	0	—	—	—	—	—	
3617·44	1	0	—	—	—	—	—	
3618·88	6	2	Fe	3618·92	10	8	20	
3619·54	6	2	Ni	3619·54	15	20	8	
3620·56	1	0	—	—	—	—	—	
3621·38	2	2	Co	3621·31	10	0	2	
3622·23	2	0	Fe	3622·15	3	6	6	
3623·37	2	0	Fe	3622·36	2	6	5	
3624·03	2	1	Zr	3624·06	8	4	1	
3624·97	9	4	Ti	3624·98	15	5	5	
3625·78	2	0	—	—	—	—	—	
3626·29	1	0	—	—	—	—	—	
3627·00	1	0	—	—	—	—	—	
3627·91	1	0	—	—	—	—	—	3627·9 (EVERSHED).

Spectrum of chromosphere.			Probable identification.					
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			
					Spark.	Arc.	Sun.	
3628·89	5	2	Y	3628·85	10	7	2	
3629·60	2	0	—	—	—	—	—	
3630·13	3	1	Zr	3630·16	5	1	1	
3630·88	8	4	Sc	3630·88	100	3	4	
3631·64	9	2	Fe	3631·61	10	6n	15	
3631·90	1	0	—	—	—	—	—	Possibly enh. Cr.
3633·26	9	2	Y	3633·28	30	4	2	
3633·62	2	1	Zr	(3633·70)	6	—	—	
3634·41	4	1	He	(3634·39)	2	—	—	
3635·55	3	1	Ti	3635·61	8	9	4	Identified in sun as Ti, Fe.
3636·69	2	0	Zr	3636·62	4	1	1	
3637·42	1	0	—	—	—	—	—	
3639·66	2	1	Pb	3639·66	20	10	1	
3640·50	3	1	Fe Cr	3640·54	5 2	6 —	6	
3641·45	11	4	Ti	3641·47	20	4	4	
3641·96	1	0	Cr	3641·97	4n	—	1	
3642·92	11	4	Sc	3642·91	50	3	2	
3643·27	2	1	—	—	—	—	—	
3643·90	4	1	—	3643·95	—	—	3	
3644·51	1	0	—	—	—	—	—	As one line, 3644·74, intensity, 1 on another photo.
3644·80	1	0	—	—	—	—	—	
3645·48	9	3	Sc	3645·47	15	1	3	
3646·32	2	0	Ti Gd	3646·34 (3646·36)	4 12	5 —	1 —	
3647·29	1	0	—	—	—	—	—	
3647·92	6	2	Fe	3647·99	9	8	12	
3649·66	3	1	Fe La	3649·65	4 1	4 5	5	Probably Fe.
3650·50	2	1	Cr	(3650·50)	5	0	—	
3651·64	1	1	Fe	3651·62	4	6	7	
3651·89	7	3	Sc	3651·94	20	1	4	
3654·07	1	0	—	—	—	—	—	
3654·78	1	0	—	—	—	—	—	
3655·14	1	0	—	—	—	—	—	
3655·93	3	1	—	—	—	—	—	
3656·39	1	1	—	—	—	—	—	
3658·17	2	0	—	—	—	—	—	
3658·87	2	0	—	—	—	—	—	
3659·88	7	3	Ti	3659·90	15	4	5	Identified in sun as Fe, Ti.
3660·73	1	0	Ti	3660·77	4	6	2	
3661·39	3	1	$H_{\epsilon'}$	(3661·35)	—	—	—	
3662·35	8	3	Ti	3662·38	15	5	5	
3663·05	2	1	—	3662·98	—	—	4	Identified in sun as Fe, Cr.
3663·58	6	2	$H_{\gamma'}$	(3663·54)	—	—	—	

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Intensity.			Spark.	Arc.	Sun.	
3664·78	8	3	Y	3664·76	20	8	2	
3665·33	1	0	—	—	—	—	—	
3666·21	7	2	$H_{a'}$	(3666·24)	—	—	—	
3667·25	2	1	—	—	—	—	—	
3667·89	8	2	H_{ω}	(3667·82)	—	—	—	
3668·61	1	0	Zr	3668·60	4	0	00	
3669·58	9	2	H_{ψ}	(3669·60)	—	—	—	
3670·62	1	1	Ni	3670·57	7	5	5	
3671·46	9	3	Zr	3671·41	8	2	0	Coincides with H_{χ} (3671·48).
3671·73	2	0	—	—	—	—	—	
3672·43	3	0	—	—	—	—	—	
3672·81	1	0	—	—	—	—	—	
3673·90	8	2	H_{ϕ}	(3673·90)	—	—	—	
3674·85	8	2	Zr	3674·87	10	3	1	
3675·85	1	0	—	—	—	—	—	
3676·54	11	3	H_{υ}	(3676·50)	—	—	—	
3677·64	2	1	—	3677·65	—	—	3	
3677·92	11	3	Cr	3677·83	6	1·5	3	}
				3677·95	8		3	
3679·50	11	3	H_{τ}	(3679·49)	—	—	—	
3680·01	4	1	Fe	3680·07	5	4	9	
3681·01	4	1	—	3681·08	—	—	3	
3681·50	1	0	—	—	—	—	—	
3682·37	2	1	Fe	3682·38	6	4	8	
3682·92	12	4	H_{σ}	(3682·95)	—	—	—	
3683·70	3	0	—	—	—	—	—	
3684·34	6	2	Fe	3684·26	4	4	7d ?	}
			Cr	(3684·39)	5	0	—	
3685·35	15	15	Ti	3685·34	50	8	10d	
3686·18	3	1	Fe	3686·14	3 2	6	6	
3687·00	11	7	H_{ρ}	(3686·97)	—	—	—	
3687·67	2	0	Fe	3687·61	6	6	6	}
				3687·80	4	6	4	
3691·70	12	8	H_{π}	(3691·70)	—	—	—	
3692·42	3	1	—	—	—	—	—	
3692·78	3	1	—	—	—	—	—	
3693·60	2	1	Co	3693·62	7	5	1	
3694·29	8	4	Yb	3694·34	200	10	3	
3695·09	4	2	—	—	—	—	—	
3695·98	1	1	—	—	—	—	—	
3696·61	1	1	—	—	—	—	—	
3697·29	12	8	H_{o}	(3697·29)	—	—	—	
3698·28	9	3	Zr	3698·30	10	0	2	
3699·15	1	1	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
Wave-length.	No. of photos.	Inten-sity.	Element.	Wave-length.	Intensity.			
					Spark.	Arc.	Sun.	
3699·86	2	1	—	3699·96	—	—	1	
3700·41	2	1	V	3700·48	6	0	1	
3701·15	2	1	Fe	3701·23	4	6	8	
3702·38	3	1	—	—	—	—	—	
3703·13	2	1	—	—	—	—	—	
3704·00	12	10	H_ξ	(3704·00)	—	—	—	
3704·75	1	0	—	—	—	—	—	
3705·09	3	1	He	(3705·15)	3	—	—	
3705·69	3	2	Fe	3705·71	6	4	9	
3706·25	11	6	Ca	3706·18	10	2	6d ?	Separate photos. range from 3706·18 to 3706·31. Compound line, but mainly Ca.
			Ti	3706·36	9	5	3	
3707·20	1	1	Fe	3707·19	2	4	5	
3707·98	3	2	Fe	3707·96	2	6	5d ?	
			—	3708·07	5		5	
3709·38	5	2	Fe	3709·39	6	6	8	
3710·43	10	6	Y	3710·43	100	7	3	
3710·97	1	0	—	—	—	—	—	
3711·40	4	2	Fe	3711·36	1	2	4	? Identification.
3712·13	13	10	H_ν	(3712·12)	—	—	—	
3713·05	6	3	Cr	3713·09	9	2	3	
3713·72	2	1	La	3713·71	6	0	—	
3714·43	2	0	—	—	—	—	—	
3714·92	4	2	Zr	3714·93	6	0	0	
3715·60	8	3	V	3715·62	10	0	4	
3716·55	2	1	Fe	3716·59	3	6	7	
3717·33	2	0	—	—	—	—	—	
3718·44	2	1	V	(3718·35)	5	0	—	3718·55, Fe, 4, in solar spectrum.
3718·95	2	1	—	—	—	—	—	
3720·08	11	6	Fe	3720·08	8	10	40	
3721·06	1	0	—	—	—	—	—	
3721·70	1	2	Ti	3721·78	8	4	4d ?	
3722·05	13	12	H_μ	(3722·08)	—	—	—	
3722·74	3	4	Fe	3722·73	6	6	6	Identified in sun as Ti, Fe.
3723·64	1	1	—	—	—	—	—	
3724·36	1	0	—	—	—	—	—	
3724·97	3	1	—	—	—	—	—	
3725·62	1	0	—	—	—	—	—	
3727·46	2	1	V	3727·49	8	0	1	
3727·78	1	1	Fe	3727·78	7	6	4	
3728·49	2	1	V	(3728·51)	5	0	—	
3728·96	1	0	—	—	—	—	—	
3729·85	2	1	Ti	3729·95	8	7	3	
3730·71	1	1	—	—	—	—	—	
3731·37	3	2	Zr	3731·40	10	0	0	Identified in sun as Co, Zr.
3732·61	1	1	Fe	3732·55	4	6	6	Identified in sun as Co, Fe.

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3732·86	5	2	V	3732·89	14	4	2	
3733·52	4	4	Fe	3733·47	6	4	7d	
3734·52	13	12	H_λ	(3734·51)	—	—	—	
3734·91	1	5	Fe	3735·01	10	8	40	Only separated from H_λ on one photo.
3735·83	2	1	Nd	(3735·76)	5	—	—	
3736·11	3	1	V	(3736·16)	5	0	—	
3737·14	12	10	Ca	3737·06	15r	3	5	Identified in sun as Ca, Mn.
			Fe	3737·28	8	8	30	
3738·37	2	3	Fe	3738·45	3	6	3	
3739·43	2	1	—	—	—	—	—	
3740·19	2	0	—	—	—	—	—	
3740·55	1	0	—	—	—	—	—	
3741·35	1	0	—	—	—	—	—	
3741·78	12	6	Ti	3741·79	30	4	4	
3743·55	6	4	Fe	3743·51	7	6	6	
3744·57	3	0	—	—	—	—	—	
3745·87	9	10	Fe	3745·72	7	8	8	Double on one photo.
				3746·06	7	6	6	
3746·99	1	0	—	—	—	—	—	
3747·72	2	1	Y	3747·69	8	—	1	
3748·38	10	7	Fe	3748·41	7	6	10	
3749·32	3	1	—	—	—	—	—	
3749·63	5	4	Fe	3749·63	10	8	20	
3750·32	13	10	H_κ	(3750·30)	—	—	—	
3751·11	2	1	—	—	—	—	—	
3751·79	4	2	Zr	3751·80	10	0	00	
3752·75	4	1	—	—	—	—	—	
3753·79	2	0	Fe	3753·73	3	4	6d ?	Identified in sun as Fe, Ti.
3754·71	2	1	Cr	3754·72	5	0	1	
3755·69	2	1	—	—	—	—	—	
3756·72	1	0	—	—	—	—	—	
3757·84	11	5	Ti	3757·82	10	5	4	
3758·44	6	4	Fe	3758·38	8	8	15	
3759·44	13	12	Ti	3759·45	50	7	12d ?	
3760·44	3	3	Fe	3760·20	3	4	5	Double on one photo.
				3760·68	2	4	4	
3761·47	13	12	Ti	3761·46	50	7	7	
3762·95	1	1	—	—	—	—	—	
3763·92	4	7	Fe	3763·95	7	8	10	
3764·29	1	0	—	—	—	—	—	
3764·81	1	0	—	—	—	—	—	
3765·65	1	3	Fe	3765·69	5	8	6	
3766·64	3	1	—	—	—	—	—	
3766·94	1	1	Zr	3766·96	10	0	1	
3767·30	4	6	Fe	3767·34	7	8	8	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3768·46	6	3	Gd	3768·54	20	20	0	
3769·66	4	3	Ni	3769·60	10	2	3	
3770·79	13	15	H_ι	(3770·77)	—	—	—	
3771·06	1	0	V	3771·12	10	0	2	
3771·83	1	1	Ti	3771·80	7	5	2	Identified in sun as Ti, C.
3773·58	1	0	—	—	—	—	—	
3774·45	10	8	Y	3774·47	100	5	3	
3775·69	1	1	Ni	3775·72	5	4	7	
3776·22	4	1	Ti	3776·20	8	2	2	
3776·72	1	0	Y	3776·70	8	—	1	Identified as Mn in sun.
3777·91	3	1	—	—	—	—	—	
3778·56	1	0	Fe	3778·46	1	4	3	
				3778·65	—	—	2	
3779·61	2	0	Fe	3779·57	1	6	4	
				3779·66	—	—	2	
3780·75	1	1	—	3780·84	—	—	3	
3781·63	1	0	—	—	—	—	—	
3782·45	2	1	Gd	(3782·49)	12	—	—	
3783·42	5	1	—	3783·48	—	—	2	
3783·60	1	2	Ni	3783·67	5	6	6	
3783·96	2	1	—	—	—	—	—	
3784·57	1	0	—	—	—	—	—	
3785·42	3	1	—	—	—	—	—	
3785·98	1	0	Fe	3786·09	3	4	3	
3786·29	1	0	Fe	3786·31	2	4	4d ?	
3786·88	1	0	Fe	3786·82	2	4	5	
3787·34	1	1	V	(3787·39)	8	0	—	
3787·96	2	3	Fe	3788·05	5	6	9	
3788·86	9	5	Y	3788·84	30	5	2	
3790·19	1	3	Fe	3790·24	3	6	5	
3790·97	1	2	La	3790·97	50	6	1	Identified in sun as La-Ca.
3792·58	2	2	—	—	—	—	—	
3793·82	3	1	—	—	—	—	—	
3795·13	1	3	Fe	3795·15	8	6	8	
3796·44	1	1	—	—	—	—	—	
3797·00	1	1	–C	3797·03	—	—	2	
3798·06	13	19	H_θ	(3798·04)	—	—	—	
3799·71	2	4	Fe	3799·69	7	6	7	
3800·15	5	2	—	—	—	—	—	
3801·02	1	0	—	—	—	—	—	
3801·62	7	2	Ce	3801·68	8	—	0	Line in sun identified –C.
3803·13	5	2	C	3803·14	—	—	2	Different photos. discordant 3802·98, 3803·21, 3803·17, 3803·09, 3803·02 ? d, and 3803·32.
3805·71	2	1	—	—	—	—	—	
3806·35	2	1	—	—	—	—	—	
3807·38	1	1	Ni	3807·29	7	5	6	

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Intensity.			Spark.	Arc.	Sun.	
3809·63	3	1	Mn	3809·72	6	5	4	
3810·79	4	1	—	—	—	—	—	
3811·45	2	1	—	—	—	—	—	
3812·17	3	1	—	—	—	—	—	
3813·17	2	4	Fe	3813·10	8	5	5	
3813·57	2	2	Ti	3813·54	4	1	2	
3814·67	7	6	Ti	3814·70	5	4	8	Identified in sun as Fe, C. LOCKYER identifies line in chromosphere as Ti.
3816·00	7	6	Fe	3815·99	9	8	15	
3817·69	2	0	—	—	—	—	—	
3818·49	2	0	Y	3818·49	10	—	1	
3819·39	2	0	—	—	—	—	—	
3819·73	3	1	He	(3819·75)	4	—	—	
3820·59	7	7	Fe	3820·59	9	8	25	Identified in sun as Fe, C.
3821·27	1	0	Fe	3821·33	4	4	4	
3821·88	2	1	—	—	—		—	
3823·47	1	0	—	—	—	—	—	
3824·02	1	0	—	—	—	—	—	
3824·58	5	7	Fe	3824·59	7	8	6	
3825·45	2	0	—	—	—	—	—	
3826·02	6	8	Fe	3826·03	9	8	20	
3826·97	1	0	–C	3826·99	—	—	2	
3828·00	5	7	Fe	3827·98	9	8	8	
3829·13	1	0	—	—	—	—	—	
3829·51	10	10	Mg	3829·50	200	30	10	
3830·60	2	2	—	—	—	—	—	Also single line at 3830·87 on five other photos.
3831·12	2	2	C	3831·17	—	—	3d	
3832·15	1	1	—	—	—	—	—	
3832·46	11	16	Mg	3832·45	200	50	15	
3833·20	3	1	—	—	—	—	—	
3833·79	1	0	—	—	—	—	—	
3834·33	7	3	Fe	3834·36	8	8	10	
3835·53	13	20	H_η	(3835·53)	—	—	—	
3836·62	1	5	C	3836·64 3836·69	— —	— —	1 1	A single line 3836·82 on five photos.
3836·92	1	4	Zr	3836·91	12	0	1	
3837·50	1	1	—	—	—	—	—	
3838·43	13	10	Mg	3838·44	500	100	25	Identified in sun as Mg-C.
3839·33	2	1	Fe	3839·40	4	6	3	
3839·99	1	0	—	—	—	—	—	
3840·54	4	3	Fe	3840·58	8	8	8	Identified in sun as Fe, C.
3841·20	4	3	Fe Mn	3841·20	8 6	8 8	10	
3842·05	4	1	—	—	—	—	—	
3843·24	4	2	Zr	3843·20	8	0	2	Identified in sun as Fe-C.
3844·39	2	1	C	3844·38	—	—	4d ?	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3845·47	2	1	—	—	—	—	—	
3846·88	2	1	Fe	3846·94	3	6	5	
3847·56	1	0	—	—	—	—	—	
3848·22	3	0	Ti	3848·14	6	4	1	
3848·94	3	1	—	—	—	—	—	
3850·12	2	2	Fe	3850·12	6	8	12	
3850·91	3	1	Fe	3850·96	3	6	4	
3851·69	2	0	—	—	—	—	—	
3852·64	1	2	—	—	—	—	—	
3853·61	1	1	—	—	—	—	—	
3854·41	1	1	—	—	—	—	—	
3854·84	3	1	C	3854·71 3854·99	— —	— —	2 1	Fourth edge of C. band.
3855·87	1	1	—	—	—	—	—	
3856·52	6	4	Fe	3856·52	8	8	8	
3857·10	1	0	—	—	—	—	—	
3858·35	4	1	Ni	3858·44	8	20	7	
3858·70	1	2	—	—	—	—	—	
3859·34	2	1	—	—	—	—	—	
3860·10	8	5	Fe	3860·06	9	10	20	
3861·03	1	2	—	—	—	—	—	
3861·71	4	2	C	3861·98	—	—	1N	Third edge of C. band.
3862·79	4	2	Si	(3862·80)	4	—	—	
3863·66	2	1	—	—	—	—	—	
3864·64	1	0	—	—	—	—	—	
3865·72	3	1	Fe	3865·67	6	8	7	
3867·60	1	1	He	(3867·61)	2	—	—	Broad.
3870·93	1	1	—	—	—	—	—	Broad band? Several lines.
3871·43	3	1	C	3871·53	—	—	2d?	Second edge of C. band.
3872·63	1	1	Fe	3872·64	6	8	6	
3873·21	2	1	Co	3873·22	15	10	2	
3873·85	2	0	Fe	3873·90	4	6	4	
3876·30	3	1	—	—	—	—	—	
3877·26	2	1	—	—	—	—	—	
3878·73	5	4	Fe	3878·72	8	8	7Nd?	
3880·53	1	1	C	3880·53	—	—	2	
3882·51	3	2	C–	3882·44	—	—	2	
3883·38	3	3	C	3883·41 3883·53	— —	— —	2 1N	Broad. First edge of C. band.
3884·53	1	0	Fe	3884·52	2	4	2	
3885·50	2	0	—	—	—	—	—	
3886·49	9	4	Fe	3886·43	8	6	15	
3887·18	1	2	Fe	3887·20	5d?	6	7	
3887·95	2	0	—	—	—	—	—	
3888·72	1	3	He	(3888·79)	10	—	—	Separated on one photo.
3889·15	13	20	H_ζ	(3889·20)	—	—	—	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3890·30	1	1	—	—	—	—	—	
3891·06	7	2	—	—	—	—	—	
3892·08	3	1	Fe	3892·07	1	0	4	
3892·29	1	0	—	—	—	—	—	
3893·09	2	1	—	—	—	—	—	
3893·46	3	1	Fe	3893·45	3	4	2	? Identification.
3894·25	2	1	Co	3894·24	30	10	5	
3894·98	1	0	—	—	—	—	—	
3895·81	5	3	Fe	3895·80	5	6	7	
3896·36	2	1	Er	(3896·42)	6	15	?	
3898·11	1	0	Fe	3898·03	2	2	3	
3899·84	4	3	Fe	3899·85	6	6	8	
3900·67	9	7	Ti	3900·68	50	6	5	Identified in sun as Ti, Fe.
3901·74	1	0	—	3901·74	—	—	1	
3902·18	1	0	—	3902·11	—	—	1	
3903·04	2	1	Fe	3903·09	7	8	10	Identified in sun as Cr, Fe.
3905·63	2	0	Si	3905·66	5	15	12	
3906·03	2	0	Nd	3906·04	4	—	3	
3906·53	2	0	—	—	—	—	—	
3907·28	6	2	Eu	(3907·3)	30	—	—	
3908·54	6	2	—	—	—	—	—	
3911·29	2	0	Nd	3911·32	7	—	0	
3912·46	2	1	—	—	—	—	—	
3912·71	1	0	—	—	—	—	—	
3913·61	10	7	Ti	3913·61	30	6	5d ?	Identified in sun as Ti, Fe.
3914·58	6	2	Zr	3914·57	4	0	1	
3915·20	1	0	—	—	—	—	—	
3916·21	5	2	La	3916·21	10	0	0	Identified in sun as Zr-La.
3918·05	1	0	—	—	—	—	—	
3918·48	3	1	Fe	3918·46	4	4	4	
3919·24	1	1	Cr	3919·31	8	3	3	
3919·97	1	0	—	—	—	—	—	
3920·39	5	2	Fe	3920·41	5	6	10	
3921·84	1	1	—	—	—	—	—	
3923·09	5	2	Fe	3923·05	6	8	12d ?	
3924·16	1	0	—	—	—	—	—	
3926·00	2	0	Fe	3925·79 3926·09 3926·16	2	4	5 4 3	
3927·28	1	1	—	—	—	—	—	
3928·10	5	4	Fe	3928·08	7	8	8	
3929·35	1	0	La	3929·36	15	0	2	Fe, Mn, La, Co, in sun.
3930·46	5	4	Fe	3930·45	6	8	8	
3931·47	1	2	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			
					Spark.	Arc.	Sun.	
3932·14	3	3	Ti	3932·16	6	0	1	
3933·84	13	100	Ca	3933·83	1000	100	1000	
3937·34	1	1	—	—	—	—	—	
3938·42	7	2	—	3938·44	—	—	2	Identification —, Cr in sun.
3939·63	1	1	—	—	—	—	—	
3940·62	1	0	—	—	—	—	—	
3941·57	1	0	Cr Nd	3941·64	5 8	—	3	
3942·63	2	0	Fe	3942·56	2	6	5	
3944·14	7	3	Al	3944·16	20	800	15	
3945·38	4	1	—	3945·36	—	—	1	
3946·59	4	1	—	—	—	—	—	
3947·98	2	0	Ti	3947·93	10	5	2	
3949·22	6	2	La	3949·20	50	6	1	
3949·72	1	1	—	—	—	—	—	
3950·45	5	2	Y	3950·50	20	5	2	
3951·78	1	0	Y	3951·77	3	—	0kd ?	
3952·36	4	1	Nd	3952·34	3	—	0	
3952·82	1	0	Fe	3952·80	2	6	4 3	
3956·60	4	1	Ti Fe	3956·48 3956·82	9 4	8 6	4 8	Identified in sun as Ce, Co Ti.
3958·29	8	2	Ti Zr	3958·36	10 15	7 8	5	
3959·43	2	0	—	—	—	—	—	
3960·51	2	0	—	—	—	—	—	
3961·64	8	5	Al	3961·67	20	1000	20	
3964·04	2	1	—	—	—	—	—	
3964·66	1	1	Ti p He	3964·42 (3964·88)	2 4	5 —	2 —	
3965·16	4	1	—	—	—	—	—	
3967·15	2	1	—	—	—	—	—	
3968·60	13	70	Ca	3968·63	500	80	700	
3970·21	13	30	H_ϵ	3970·18	—	—	—	
3972·02	5	2	Eu	3972·13	50	50	0 ?	
3973·32	4	1	—	—	—	—	—	
3974·29	2	1	—	—	—	—	—	
3975·14	1	0	—	—	—	—	—	
3975·64	2	1	—	—	—	—	—	
3977·34	1	0	—	—	—	—	—	
3979·01	1	0	—	—	—	—	—	
3980·01	1	0	—	—	—	—	—	
3981·87	2	2	Ti	3981·92	15	9	4	A very broad band extending from 3981·8 to 3982·7. On two photos. lines are separated. There is probably another line between Ti and Y.
(3982·59)	(4)	(3)	—	—	—	—	—	
3982·75	2	2	Y	3982·74	20	6	3	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
3984·13	3	1	Cr	3984·06	7	5	3	Probably Fe.
			Fe	3984·11	3	6	4	
3988·67	8	2	La	3988·66	30	5	0	
3990·11	6	2	Ti	3989·91	20	8	4	Not entirely due to Ti. The line 3990·13 identified as Mn-Cr in the sun.
			—	3990·13	—	—	1	
3990·42	1	1	—	—	—	—	—	
3991·42	5	2	Cr	3991·33	9	4	3	
			Zr		15	8		
3991·85	2	1	Co	3991·87	8	2	2	
			Cr		2	3		
3992·50	2	1	—	—	—	—	—	
3993·03	2	0	Cr	3992·97	5	3	3d ?	
			V		12	6		
3994·14	1	0	—	—	—	—	—	
3994·87	3	2	Nd	3994·83	5	—	2	
3995·90	6	2	La	3995·90	5	5	1Nd	
3996·48	1	1	—	—	—	—	—	
3997·09	3	1	—	—	—	—	—	
3997·95	2	1	Co	3998·05	10	9	4d ?	
3999·28	9	6	Zr	3999·12	15	0	1	Identified in sun as Zr, Fe.
			V	3999·37	6	0	0	
4000·51	5	1	—	—	—	—	—	
4002·75	1	1	Fe	4002·65	1	1	0d	Identified in sun as Fe, Ti.
4003·62	1	0	Cr	(4003·48)	5	0	—	
4004·13	2	1	—	—	—	—	—	
4004·84	2	0	—	—	—	—	—	
4005·44	1	2	Fe	4005·41	8	8	7	
4005·86	2	1	V	4005·86	20	0	3	
4006·70	1	0	—	—	—	—	—	
4007·51	2	0	Fe	4007·43	2	4	5	
4008·16	1	0	—	—	—	—	—	
4008·92	3	1	—	—	—	—	—	
4009·85	1	0	Fe	4009·86	3	6	3	
4010·47	1	1	—	—	—	—	—	
4011·41	1	0	—	—	—	—	—	
4012·50	9	10	Ti	4012·54	7	2	4	
4013·77	1	1	—	—	—	—	—	
4014·77	4	1	Sc	4014·68	8	—	5d ?	
			Fe		2	2		
4015·71	3	1	—	4015·76	—	—	3	
4017·72	2	1	—	—	—	—	—	
4019·24	2	1	—	—	—	—	—	
4020·50	5	2	Sc	4020·55	8	4	1	
4021·92	6	2	Ti	4022·02	4+	6	4	Identified in sun as Ti-Fe-V.
4023·55	6	2	V	4023·53	10	1	3	Identified in sun as V Co.

Spectrum of chromosphere.			Probable identification.					
Wave-length.	No. of photos.	Inten-sity.	Element.	Wave-length.	Intensity.			
					Spark.	Arc.	Sun.	
4024·13	1	1	Zr	4024·15	3	1	1	
4024·76	3	1	Ti	4024·73	5	10	3	
4025·31	5	1	Ti	4025·29	4	2	3	
4026·52	7	2	He	(4026·34)	5	—	—	
			Ti	4026·69	4	5	1	
4027·67	1	1	—	—	—	—	—	
4028·63	8	2	Ti	4028·50	10	3	4	
4029·95	4	1	Fe	4029·78	1	1	5	
			Si	4030·1	2	—	—	
4030·87	7	2	Mn	4030·92	20	30	9	
4031·92	9	3	La	4031·87	20	7	2	
4032·73	1	1	Fe	4032·79	2	2	4	? Identification.
4033·23	4	1	Mn	4033·22	20	25	8	
4034·01	3	1	—	—	—	—	—	
4034·62	6	1	Mn	4034·64	10	20	6	
4035·87	6	1	V	(4035·77)	16	4	—	
			Mn	4035·88	8	5	4d ?	
4037·03	2	1	—	—	—	—	—	
4040·36	1	0	—	—	—	—	—	
4041·05	8	3	Nd	4040·94	7	—	1d ?	Identified in sun as Ce, Nd, Co.
4041·94	2	0	—	—	—	—	—	
4042·97	8	3	La	4043·05	20	8	0	
4045·97	7	3	Fe	4045·98	10	10	30	
4048·82	5	2	Zr	4048·82	10	7	1	
4053·85	6	1	V	4053·80	8	0	0	
			Ti	4053·98	8	3	3	
4055·18	3	1	Ti	4055·19	6	4	3	Identified in sun as Cr, Ti, Zr.
4056·67	2	1	—	—	—	—	—	
4058·02	2	1	Pb	4058·04	300	1000	0	
4059·01	1	0	—	—	—	—	—	
4061·28	5	1	Nd	4061·24	10	10	3	
4062·68	2	1	Fe	4062·60	3	8	5	
4063·75	2	2	Fe	4063·76	10	10	20	
4065·48	2	0	—	—	—	—	—	
4067·23	2	2	Ni	(4067·2)	4	0	—	
4068·88	1	0	—	—	—	—	—	
4069·33	3	1	—	—	—	—	—	
4071·8	3	2	Fe	4071·91	10	10	15	Very diffused.
4073·8	3	2	Fe	4073·92	2	4	4	Very diffused. ? Identification.
4075·42	3	1	—	—	—	—	—	
4076·03	6	2	—	4076·10	—	—	3	
4077·86	9	15	Sr	4077·89	1000	10	8	
4078·66	2	3	Ti	4078·63	7	6	3	
4079·84	1	2	—	—	—	—	—	
4080·62	1	2	—	—	—	—	—	
4081·46	1	2	Zr	4081·39	10	5	0	Possibly Sc.

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4082·62	2	1	Ti	4082·59	3	7	5	Solar line Sc-Ti-Fe.
4083·52	5	2	—	—	—	—	—	
4084·60	1	1	—	—	—	—	—	
4085·63	1	1	—	—	—	—	—	
4086·88	6	4	La	4086·86	20	10	1	
4087·82	3	1	—	—	—	—	—	
4089·01	3	2	Si	(4089·1)	2	—	—	? Identification.
4089·57	1	0	—	—	—	—	—	
4090·06	2	2	—	—	—	—	—	
4090·78	3	2	V	4090·73	8	5	1	
4092·87	4	2	V	4092·82	15	3	3d ?	
			Ca		1	4	—	
4094·56	1	2	—	—	—	—	—	
4095·58	1	0	V	4095·63	6	5	0	
4097·05	1	0	Si	(4096·9)	1	—	—	
4099·09	1	1	—	—	—	—	—	
4100·16	1	1	—	—	—	—	—	
4101·92	7	30	H_δ	—	—	—	—	
4103·15	1	2	Si	4103·10	1	—	5	Identified in sun as Si, Mn.
4105·09	3	2	La	4105·10	1	10	1	? Identification.
4106·61	1	1	—	—	—	—	—	
4107·58	5	1	Fe	4107·65	4	8	5	Identified in sun as Ce-Fe.
4109·61	6	4	Nd	4109·61	8	—	1	
4110·64	2	1	Co	4110·69	10	8	4	
4112·14	2	1	—	—	—	—	—	
4113·07	1	0	—	—	—	—	—	
4114·13	3	2	—	—	—	—	—	
4115·43	2	1	—	—	—	—	—	
4116·66	1	1	—	—	—	—	—	
4118·58	4	2	Fe	4118·71	5	10	5	
4119·37	1	1	—	—	—	—	—	
4120·10	3	1	—	—	—	—	—	
4121·27	2	1	He	(4120·97)	—	—	—	
			Co	4121·48	10	4	6d ?	Identified in sun as Cr-Co.
4122·70	3	1	Fe	4122·67	2	6	3	
4123·56	6	3	La	4123·38	30	10	1	Double on one photo., 4123·45 and 4124·01.
			Ti	4123·70	5	5	0	
4125·05	6	2	Y	4125·06	6	—	1	
4126·22	1	2	—	—	—	—	—	
4127·67	4	2	Ti	4127·69	7	5	0	
4128·31	4	2	Si	4128·21	5	—	—	Identified in sun as Ce-V.
			V	4128·25	10	7	6d ?	
4128·93	1	0	—	—	—	—	—	
4129·87	5	4	Eu	4129·88	100	100	1	
4130·97	6	2	—	—	—	—	—	
4131·93	1	0	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave length.	No. of photos.	Intensity.			Spark.	Arc.	Sun.	
4132·59	3	1	Fe	4132·23	6	8	10	
			—	4132·69	—	—	3	
4133·08	1	0	Fe	4133·06	4	8	4	
4133·83	4	1	Ce	4133·97	8	10	0	Measures discordant, 4133·73, 4133·75, 4134·01, 4133·84.
4134·81	3	1	Fe	4134·84	5	10	5	
4135·58	7	2	—	—	—	—	—	
4137·54	7	3	—	4137·57	—	—	2	
4138·62	1	0	—	—	—	—	—	
4143·27	2	1	Nd	4143·30	8	—	—	On four photos. there are two bright lines separated by an absorption line.
4143·91	1	1	p He	4143·92	2	—	—	
			Fe	4144·04	7	10	15	
4143·27	4	3	—	—	—	—	—	
4144·04	Absn.	line	—	—	—	—	—	
4144·88	4	2	—	—	—	—	—	
4146·36	4	2	—	—	—	—	—	
4149·33	6	3	Zr	4149·36	20	10	2	
4150·10	4	2	Ce	4150·06	10	—	00	
4151·07	5	2	Ti	4151·13	5	5	1	
			Zr		6	4		
4152·14	5	2	La	4152·11	10	8	2	Identified in sun as Fe, La. Possibly Ce.
4153·96	1	1	Fe	4154·07	2	4	4	
4154·71	4	1	Fe	4154·67	4	6	4	
				4154·98	3	6	4	
4155·66	2	1	—	—	—	—	—	
4156·33	7	5	Nd	4156·24	10	—	0	
			Zr	4156·39	10	8	1	
4157·26	2	1	—	—	—	—	—	
4158·05	3	1	Fe	4157·95	2	6	5	
4161·51	4	3	Zr	4161·37	10	7	2	
			Ti	4161·68	2	2	4	
4162·73	1	1	—	—	—	—	—	
4163·80	5	4	Ti	4163·82	20	2	4	Identified in sun as Ti-Cr.
4164·43	2	1	—	—	—	—	—	
4165·71	3	2	Ce	4165·76	10	4	1	
4166·93	1	0	—	—	—	—	—	
4167·42	3	3	—	4167·44	—	—	8	Very broad. ? Double.
4168·80	1	0	—	—	—	—	—	
4169·58	1	0	—	—	—	—	—	
4169·95	3	1	—	—	—	—	—	
4170·89	2	1	—	—	—	—	—	
4172·05	7	3	Ti	4172·07	10	1	2	
4172·81	1	0	—	—	—	—	—	
4173·53	8	5	Fe	4173·53	2	1	1	
4174·48	2	1	—	—	—	—	—	
4175·62	3	1	Fe	4175·81	4	8	5	Wave-length of arc line 4175·71 (K. and R.).

Spectrum of chromosphere.			Probable identification.					
			Element.	Wave-length.	Intensity.			
Wave-length.	No. of photos.	Inten-sity.			Spark.	Arc.	Sun.	
4176·56	3	1	—	—	—	—	—	
4177·66	9	6	Y	4177·70	50	5	3	
4179·03	9	6	Fe	4179·03	2	1	3	
4179·69	3	2	—	—	—	—	—	
4181·01	2	0	C	4180·97	—	—	2N	
4183·53	1	1	—	—	—	—	—	
4184·32	1	1	—	—	—	—	—	
4186·76	1	1	Ce	4186·78	10	—	2N	Identified in sun as Ce-Zr.
4188·18	2	0	—	—	—	—	—	
4188·32	1	0	—	—	—	—	—	
4192·61	1	1	—	—	—	—	—	
4193·45	3	1	—	—	—	—	—	
4194·08	1	0	—	—	—	—	—	
4194·58	1	0	—	—	—	—	—	
4195·10	1	0	—	—	—	—	—	
4195·52	1	1	Fe	4195·49	3	6	5	
4196·75	3	2	La	4196·70	10	0	2	
4197·15	1	1	—	—	—	—	—	
4198·15	2	1	—	—	—	—	—	
4198·73	1	0	—	—	—	—	—	
4199·18	3	1	Fe	4199·27	8	10	5	Identified in sun as Zr-Fe.
4200·73	1	1	—	—	—	—	—	
4202·10	2	2	Fe	4202·20	9	10	8	
4203·35	2	1	—	—	—	—	—	
4205·21	4	6	Eu	4205·19	100	50	1	
4206·57	2	1	—	—	—	—	—	
4209·15	3	2	Zr	4209·14	10	0	1	
4211·46	1	1	—	—	—	—	—	
4212·17	3	1	Zr	4212·05	5	0	2	
4215·71	5	12	Sr	4215·70	100	10	5d ?	
4217·22	1	0	—	—	—	—	—	
4217·57	3	0	—	—	—	—	—	
4218·61	1	0	Zr	4218·56	2	0	1Nd	
4220·43	1	0	—	—	—	—	—	
4220·73	1	0	—	—	—	—	—	
4222·72	1	1	—	—	—	—	—	
4223·08	3	2	—	—	—	—	—	
4225·49	3	2	V	(4225·41)	4	1	—	
4226·85	4	6	Ca	4226·90	100	75	20d ?	
4227·42	1	1	Fe	4227·61	7	10	4	? Enh. Ti, 27·40 (L).
4231·96	1	0	Zr	4231·86	6	0	1	
4232·60	3	1	—	—	—	—	—	
4233·36	5	7	Fe	4233·33	4	1	4	
4235·40	1	1	Mn	4235·30 4235·45	20	10 10	2 3	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4236·04	3	1	Fe	4236·11	8	10	8	
4236·93	1	1	—	—	—	—	—	
4237·75	1	0	—	—	—	—	—	
4238·28	1	0	—	—	—	—	—	
4238·51	1	1	La	4238·55	10	10	1Nt	
4238·91	1	1	Fe	4238·97	4	8	5	
4240·13	1	0	—	—	—	—	—	
4242·53	2	1	Cr	4242·54	8	1	2	
4243·59	3	1	—	—	—	—	—	
4244·93	2	0	—	—	—	—	—	
4247·00	5	10	Sc	4247·00	100	10	5	
4248·92	2	1	—	—	—	—	—	
4250·19	2	1	Fe	4250·29	7	10	8	
4250·85	1	0	Fe	4250·95	8	10	8	
4251·82	1	1	—	—	—	—	—	
4254·51	5	3	Cr	4254·51	50	50	8	
4256·31	2	1	—	—	—	—	—	
4258·24	3	2	Zr	4258·20	7	5	0	
4260·51	2	2	Fe	4260·64	10	10	10	
4262·14	3	2	Cr	4262·14	4	0	1	
4271·87	3	2	Fe	4271·93	10	10	15	
4273·02	1	0	—	—	—	—	—	
4273·55	2	2	—	—	—	—	—	
4274·99	5	3	Cr	4274·96	30	50	7	
4275·71	3	1	—	—	—	—	—	
4280·39	1	0	—	—	—	—	—	
4282·76	3	2	—	—	—	—	—	
4284·13	1	0	—	—	—	—	—	
4285·96	1	0	—	—	—	—	—	
4286·48	1	0	—	—	—	—	—	
4287·29	1	0	La	4287·16	20	10	2	Identification doubtful
4288·10	4	2	Ti	4288·04	2	1	2	
4289·06	1	1	—	—	—	—	—	
4289·77	1	1	Cr	4289·89	30	15	5	On one photo. 4289·77, intensity 1; 4290·32, intensity 5. On the others only one line.
4290·21	5	5	Ti	4290·37	9	5	2	
4291·19	2	1	Ti	4291·11	4	3	3	
				4291·28	4	3	2	
4292·14	2	1	—	—	—	—	—	
4293·09	2	1	—	—	—	—	—	? Double.
4294·22	5	2	Ti	4294·20	10	5	2	
4295·20	2	1	—	—	—	—	—	
4296·11	2	1	Ti	4295·91	4	10	3	Identified in sun as Cr-Ti.
			La	4296·24	10	8	0N	
4296·83	4	4	Fe	4296·74	1	—	3	
			Zr	4296·84	5	—	1	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4298·03	2	1	—	—	—	—	—	
4298·72	1	1	—	—	—	—	—	As a single line 4298·86 on another photo.
4299·07	1	1	—	—	—	—	—	
4300·22	5	5	Ti	4300·21	8	5	3	
4300·70	1	0	Ti	4300·73	4	7	2	
4301·17	1	1	Ti	4301·17	6	7	2	
4302·07	3	2	Ti	4302·09	6	2	2	
4302·55	2	1	—	—	—	—	—	
4302·94	1	3	—	—	—	—	—	
4303·51	4	3	Fe	4303·34	2	1	2	4303·63, 4303·52 br, 4303·43 ? d, 4303·44, are separate results.
				4303·58	—	—	1N	
4305·30	1	1	—	—	—	—	—	
4305·83	2	3	Sr	4305·61	30	6	3	Identified in sun as Fe, Cr, Sr, Ti.
			Ti	4306·08	15	15	4	
4308·02	4	4	Ca	4307·91	20	3	3	
			Fe	4308·08	10	10	6	
4309·86	4	2	Y	4309·79	20	6	1	
4312·54	1	1	—	—	—	—	—	
4313·02	5	2	Ti	4313·03	8	2	3	
4314·31	4	2	Sc	4314·25	30	3	3	
4315·13	5	3	Ti	4315·14	7	4	3	
4317·29	2	1	—	—	—	—	—	
4319·03	2	1	—	—	—	—	—	
4320·98	5	4	Sc	4320·91	20	3	3	
			Ti	4321·12	2	1	2	
4323·15	1	0	—	—	—	—	—	Diffused.
4323·72	1	1	—	—	—	—	—	
4325·25	2	1	Sc	4325·15	20	3	4	
4325·88	5	4	Fe	4325·94	10	10	8	
4329·20	2	1	—	—	—	—	—	
4330·58	4	2	Ti	4330·40	2	3	1	
				4330·87	2		2	
4331·47	1	1	—	—	—	—	—	
4333·05	1	1	V	4332·90	12	6	0	? Identification.
4333·98	3	3	La	4333·93	15	15	1N	
4335·49	1	0	—	—	—	—	—	
4336·12	1	0	—	—	—	—	—	
4336·70	2	0	—	—	—	—	—	
4338·05	5	5	Ti	4338·08	10	6	4	
4340·65	5	100	H_γ	4340·64	—	—	20	
4342·85	1	0	—	—	—	—	—	
4343·74	1	0	—	—	—	—	—	
4344·55	3	2	Ti	4344·45	2	1	2	
			Cr	4344·67	10	7	4	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4346·40	2	0	—	4346·45	—	—	1	
4348·06	3	1	Zr	4348·13	8	3	1	
4350·00	2	0	—	—	—	—	—	
4352·00	4	4	Fe	4351·93	4	2	—	
			Cr	4351·93	10	9	5	
			Mg	4352·08	4	8	5	
4353·10	2	0	V	4353·04	12	7	0	
4354·61	3	1	—	—	—	—	—	
4356·28	2	1	—	—	—	—	—	
4358·39	2	1	—	—	—	—	—	
4358·89	3	1	Y	4358·88	8	5	0	
4359·82	3	2	Cr	4359·78	7	8	3	
			Zr	4359·90	10	8	0	
4364·77	3	2	Ce	4364·83	4	—	0	? Identification.
4366·71	1	2	—	—	—	—	—	
4367·85	2	2	Ti	4367·84	6	3	2	
4369·86	2	2	Fe	4369·94	3	8	4	
4371·32	3	2	—	4371·24	—	—	1	
			Cr	4371·44	7	10	2	
4372·59	2	1	—	—	—	—	—	
4373·97	1	1	—	—	—	—	—	
4375·14	4	7	Y	4375·10	100	8	2	
4379·94	1	2	Zr	4379·93	12	7	0	
4383·72	3	5	Fe	4383·72	10	10	15	
4385·63	3	4	Fe	4385·55	1	0	2	
4387·01	2	1	Ti	4387·01	5	2	1	
4388·17	2	1	p He	(4388·10)	5	—	—	
4390·28	1	1	—	—	—	—	—	
4391·03	3	2	—	—	—	—	—	
4391·99	3	1	—	—	—	—	—	
4393·34	1	0	—	—	—	—	—	
4394·08	2	1	—	—	—	—	—	
4395·24	4	8	Ti	4395·20	15	8	3	
4398·20	3	2	Y	4398·18	15	5	1	
4399·90	3	2	Ti	4399·94	10	2	3	Identified in sun as Ti-Cr.
4400·67	3	3	Sc	4400·56	20	3	3	
4401·49	1	1	—	—	—	—	—	
4403·49	2	2	Zr	4403·53	4	1	0	
4404·51	1	0	—	—	—	—	—	
4404·89	2	1	Fe	4404·93	10	10	10	
4406·66	1	0	—	—	—	—	—	
4408·97	2	3	—	—	—	—	—	Broad band.
4411·15	2	2	Ti	4411·24	6	0	1	Identified in sun as – Cr.
4412·33	2	1	—	—	—	—	—	
4413·93	1	1	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4415·17	1	1	Fe	4415·29	8	10	8	
4415·65	2	2	Sc	4415·72	15	2	3	
4416·98	2	3	—	4416·98	—	—	2	
4417·93	3	3	Ti	4417·88	6	5	3	
4418·73	1	0	—	—	—	—	—	
4421·83	2	1	Ti	4421·93	3	4	00	
4422·92	2	1	Y	4422·74	10	—	3	
4424·53	2	2	—	—	—	—	—	
4427·30	2	2	Ti	4427·27	8	10	2	
4429·41	1	1	—	—	—	—	—	
4430·08	2	2	La	4430·07	8	10	00N	
4434·30	2	1	—	—	—	—	—	
4435·53	2	2	Ca	4435·13	20	5	5	Possibly Eu 4435·7.
				4435·85	15	3	4	
4443·98	4	6	Ti	4443·98	15	3	5	
4446·55	2	3	—	—	—	—	—	
4447·93	2	1	Fe	4447·89	3R	8	6	
4449·48	2	2	Ti	4449·31	10	10	2	
4450·50	4	2	—	4450·48	—	—	1	
			Ti	4450·65	6	1	2	
4454·96	2	1	Ce	4454·95	30	8	5	
4457·48	2	1	—	—	—	—	—	
4458·51	2	1	—	—	—	—	—	
4459·65	1	0	—	—	—	—	—	
4460·37	3	1	—	—	—	—	—	
4461·44	2	1	—	—	—	—	—	
4462·45	3	1	—	—	—	—	—	
4463·31	2	1	—	—	—	—	—	
4464·65	3	1	Ti	4464·62	2	3	2	
4466·65	1	0	Fe	4466·73	5	8	5	
4468·71	5	5	Ti	4468·66	15	6	5	
4469·57	2	1	Fe	4469·55	2	8	4	
4471·51	5	7	He	(4471·65)	6	—	—	
4472·98	3	1	—	—	—	—	—	
4474·11	1	0	—	—	—	—	—	
4474·99	1	0	—	—	—	—	—	
4476·06	3	1	Fe	4476·19	5	10	4	
4479·61	1	1	—	—	—	—	—	
4481·33	2	1	Mg	4481·30	100	0	00	Separate measures, 4481·23, 4481·43.
			Ti	4481·43	7	5	1	
4482·14	2	1	Fe	4482·34	4	8	5	
4483·93	1	1	—	—	—	—	—	
4485·61	1	1	—	—	—	—	—	
4487·05	1	1	—	—	—	—	—	
4487·73	1	0	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4488·44	1	1	Ti	4488·49	7	3	1	
4489·36	4	3	Fe	4489·35	1	0	2	
4491·68	4	3	Fe	4491·57	1	0	2	
4494·37	1	1	—	—	—	—	—	
4494·87	1	1	—	—	—	—	—	
4496·87	4	2	Cr	4497·02	6	5	3	
4499·19	2	0	—	—	—	—	—	
4501·51	5	6	Ti	4501·46	15	6	5	
4505·97	1	0	—	—	—	—	—	
4507·05	1	0	—	—	—	—	—	
4508·45	4	3	Fe	4508·46	2	1	4	
4512·32	1	1	—	—	—	—	—	
4514·61	1	1	—	—	—	—	—	
4515·54	4	3	Fe	4515·51	1	1	3	
4518·51	1	2	—	—	—	—	—	
4520·41	4	4	Fe	4520·40	1	1	3	
4522·84	5	5	Fe	4522·80	2	1	3	
4527·82	1	0	—	—	—	—	—	
4528·96	2	1	Fe	4528·80	6R	10	8	
4529·79	1	0	Al	(4529·80)	10	0	—	(LOCKYER.)
4531·24	3	1	Co	4531·12	20	9	2	
			Fe	4531·33	1	3	5	
4534·18	5	6	Ti	4534·14	8	4	6	
4535·94	4	2	Ti	(4535·95)	6, 6	6, 6, 6	3, 2, 2	
4539·89	4	1	—	—	—	—	—	
4541·50	3	1	Fe	(4541·40)	3	1	—	(LOCKYER.)
4542·03	1	0	—	—	—	—	—	
4544·26	1	0	—	—	—	—	—	
4545·33	3	2	—	—	—	—	—	? Double.
4547·64	2	0	—	—	—	—	—	
4549·79	5	8	Ti	4549·81	15	4	6d ?	Identified in sun as Ti, Co.
4550·99	1	0	—	—	—	—	—	
4552·64	2	1	Ti	4552·63	4	5	2	
			Si	4552·73	8	—	1	
4554·18	5	7	Ba	4554·21	1,000	10	8	
4556·05	4	4	Fe	4556·06	1	1	3	
4558·71	5	2	Cr	4558·83	10	2	3	
4560·73	4	1	—	—	—	—	—	? Double.
4563·14	1	0	—	—	—	—	—	
4563·96	5	6	Ti	4563·94	15	4	4	
4565·82	3	2	—	—	—	—	—	
4567·02	2	0	—	—	—	—	—	
4569·22	1	1	—	—	—	—	—	
4572·20	5	7	Ti	4572·16	20	5	6	
4574·95	1	1	—	—	—	—	—	

Spectrum of chromosphere.			Probable identification.					
					Intensity.			
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	
4576·52	3	1	Fe	4576·51	1	—	2	
4577·56	2	0	—	—	—	—	—	
4578·86	2	0	—	—	—	—	—	
4580·59	3	1	V	4580·59	10	8	1	
4581·80	2	1	Co	4581·69	10	7	4	
4583·03	1	1	—	—	—	—	—	
4584 06	5	6	Fe	4584·02	4	2	4	
4586·79	1	0	—	—	—	—	—	
4588·29	3	1	Cr	4588·38	10	1	3	
4590·11	3	1	Ti	4590·13	7	1	3	
4592·55	3	1	Cr	4592·25	4	0	1	Enh. Cr (L).
				4592·71	1	0	—	
4594·19	4	1	—	—	—	—	—	
4595·77	1	1	—	—	—	—	—	
4596·95	1	1	—	—	—	—	—	
4598·34	2	0	Fe	4598·30	1	6	3	
4600·70	3	2	—	—	—	—	—	
4609 71	1	0	—	—	—	—	—	
4611·58	2	1	—	—	—	—	—	
4613 64	2	2	—	—	—	—	—	
4616 45	2	1	Cr	4616·31	7	6	4	
4619·20	2	1	Cr	4618·97	5	0	4d?	
			Cr	4619·47	5	0	3	
4620·40	2	1	—	—	—	—	—	
4622·89	3	2	—	—	—	—	—	
4624·90	1	0	—	—	—	—	—	
4626·58	1	0	—	—	—	—	—	
4629·49	3	6	Fe	4629·52	1	1	6	Identified in sun as Ti, Co, Fe.
4632·76	1	1	—	—	—	—	—	
4634·07	1	2	Cr	4634·25	6	1·5	2	
4637·90	1	1	—	—	—	—	—	
4639 88	2	3	Ti	(4639·86)	5, 4, 5	5, 5, 5	2, 2, 1	
4643·13	1	0	—	—	—	—	—	
4646·36	2	3	Cr	4646·35	7	8	5	
4648·75	2	2	Ni	4648·84	6	3	4	
4652·12	2	1	Cr	4651·46	6	7	4	
				4652·34	7	7	5	
4654·63	3	1	Fe	4654·67	—	10	4	
				4654·80	—	—	5	
4657·00	3	2	Ti	(4657·08)	6, 3	3	3, 1, 2	
4662·32	1	0	—	—	—	—	—	
4663·64	2	3	Al	(4663·70)	10	0	—	
4667·16	3	3	—	—	—	—	—	
4669·46	1	0	—	—	—	—	—	
4670·45	3	2	Sc	4670·59	7	0	2	

Spectrum of chromosphere.			Probable identification.					LORD.	
					Intensity.				
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Spark.	Arc.	Sun.	Wave-length.	Intensity.
4672·85	1	0	—	—	—	—	—		
4678·78	1	1	Fe	4679·03	1	8	6		
4680·36	1	1	Zn	4680·32	—	20	1		
4682·20	2	2	—	—	—	—	—		
4689·45	1	0	—	—	—	—	—		
4697·26	1	2	—	—	—	—	—		
4698·90	2	3	—	—	—	—	—		
4703·65	2	1	—	—	—	—	—		
4707·25	1	1	—	—	—	—	—		
4708·89	2	1	—	—	—	—	—		
4710·21	2	1	—	—	—	—	—		
4713·37	1	1	He	(4713·25)	3	—	—		
4714·47	2	2	Ni	4714·60	3	—	6		
4715·48	1	1	—	—	—	—	—		
4722·49	2	2	Zn	4722·34	—	20	3		
4728·05	2	2	—	—	—	—	—		
4731·64	2	3	Fe	4731·64	—	1	4		
4737·05	2	3	Fe	4736·96	1	10	6		
4740·42	2	1	—	—	—	—	—		
4743·45	1	1	—	—	—	—	—		
4746·04	1	0	—	—	—	—	—		
4749·58	1	1	—	—	—	—	—		
4751·87	1	0	—	—	—	—	—		
4754·46	1	0	Mn	4754·23	—	10	7		
4756·63	1	0	—	—	—	—	—		
4758·20	1	0	—	—	—	—	—		
4762·62	1	1	Mn	4762·57	—	8	5		
4764·39	1	1	—	—	—	—	—		
4766·13	1	1	Mn	4766·05 4766·62	— —	7	3 4		
4768·54	1	0	—	—	—	—	—		
4773·99	1	0	—	—	—	—	—		
4776·37	2	1	—	—	—	—	—	4776·00	1
4778·06	2	1	—	—	—	—	—	—	—
4780·39	2	1	—	—	—	—	—	4780·10	1
4783·69	2	2	Mn	4783·61	—	10	6	4783·45	1
4786·83	2	2	Y	4786·80	—	—	—	4786·52	1
4789·70	2	2	—	—	—	—	—	4789·51	1
4792·93	2	2	—	—	—	—	—	—	—
4796·18	1	0	—	—	—	—	—	—	—
4798·67	2	2	—	—	—	—	—	4798·76	1
4800·97	2	1	—	—	—	—	—	—	—
4805·30	3	3	Ti	4805·29	4	1	3	4805·16	2
4811·04	1	2	Zn	4810·72	—	20	3	4810·90	1
4815·97	1	0	—	—	—	—	—	—	—

Spectrum of chromosphere.			Probable identification.					Lord.	
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			Wave-length.	Intensity.
					Spark.	Arc.	Sun.		
4824·11	2	3	Cr	4824·33	8	1	3	4823·95	2
4829·24	1	1	—	—	—	—	—	—	—
4832·59	2	1	—	—	—	—	—	—	—
4836·53	2	1	—	—	—	—	—	—	—
4840·53	1	1	Co Fe	4840·45 4840·50	— —	9 1	2 3	— —	— —
4844·02	1	1	—	—	—	—	—	—	—
4846·71	1	1	—	—	—	—	—	—	—
4848·83	1	2	Cr	4848·44	—	1	2	4848·39	1
4849·30	1	1	—	—	—	—	—	—	—
4855·50	2	2	Ni	4855·60	—	—	3	4855·22	1
4861·53	2	100	H_β	4861·53	—	—	30	4861·51	20
4866·15	1	1	—	—	—	—	—	—	—
4868·20	2	2	—	—	—	—	—	—	—
4871·74	2	2	Fe	4871·51 4872·33	— —	8 8	5 4	4871·74	1
4881·66	2	1	—	—	—	—	—	—	—
4883·77	2	2	Y	4883·87	—	—	2	4883·74	2
4885·91	1	1	—	—	—	—	—	—	—
4891·59	2	3	Fe	4891·69	5	10	8	4891·24	2
4894·04	1	1	—	—	—	—	—	—	—
4900·26	2	4	Y	4900·30	—	6	2	4900·05	2
4904·04	1	1	—	—	—	—	—	4904·37	1
4909·94	1	0	—	—	—	—	—	4910·54	1
4911·14	1	0	Ti	4911·38	—	3	1		
4911·98	1	0	—	—	—	—	—	—	—
4913·10	1	0	—	—	—	—	—	—	—
4914·34	1	1	—	—	—	—	—	4913·91	1
4919·17	2	1	Fe	4919·17	—	8	6	4919·16	1
4921·17	2	3	Fe p He	4920·69 4922·10	12 4	9 —	10 —	4920·61	1
4924·11	2	8	Fe	4924·11	15	1	5	4924·12	5
4928·11	1	0	—	—	—	—	—	—	—
4930·87	1	1	—	—	—	—	—	—	—
4934·17	2	3	Ba	4934·25	—	100	7	4934·21	5
4938·70	2	1	Fe	4939·00	—	6	4	4938·92	1
4952·48	1	0	—	—	—	—	—	—	—
4957·58	2	2	Fe	4957·49 4957·79	2 10	6 8	5 8	4957·57	3
5013·95	1	1	—	—	—	—	—	5013·28 5014·59	1 1
5018·56	2	7	Fe	5018·63	10	3	4	5018·67	5
5022·07	1	0	—	—	—	—	—	—	—
5030·80	1	1	—	5031·20	—	—	3	5031·20	2

Spectrum of chromosphere.			Probable identification.					Lord.		
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			Wave-length.	Intensity.	
					Spark.	Arc.	Sun.			
5097·07	1	0	Fe	5097·17	—	4	3	5097·0	1	
5100·16	1	0	—	—	—	—	—	5101·0	1	
5154·44	1	0	Ti	5154·24	—	0	2	5154·12	1	
5162·93	1	0	Fe	5162·45	—	6	5	5162·05	1	
5164·25	1	1	—	—	—	—	—	—	—	
5167·70	1	0	Mg Fe	5167·50 5167·68	— 5	10 4	15 5	5167·39	5	
5169·01	2	4	Fe	5169·07 5169·22	5 10	4 2	3 4	5169·14	5	
5173·01	2	4	Mg	5172·86	—	15	20	5173·22	5	
5178·14	2	1	—	—	—	—	—	—	—	
5183·80	2	5	Mg	5183·79	—	20	30	5184·18	8	
5188·38	1	0	—	—	—	—	—	5188·78	1	
5192·98	1	0	Fe	5192·52	—	10	5	5192·10	1	
5196·80	1	0	—	—	—	—	—	5195·29 5197·56	1 1	
5205·99	2	1	Cr	5206·22	—	10	5	5205·43	1	
5219·74	1	1	—	—	—	—	—	—	—	
5227·21	2	2	Fe	5227·04	—	10	3	5226·95	1	
5234·88	2	2	—	5234·79	—	—	2	5234·42	2	
5249·80	1	0	—	—	—	—	—	5250·68	1	
5254·96	1	1	—	—	—	—	—	5254·98	1	
5265·59	1	1	Ca	5265·73	—	—	—	5261·0 5267·0 } band	1 1	
5270·03	2	1	Fe	5269·72 5270·56	— —	10 10	8d ? 4	5270·02	5	
5276·24	2	2	Fe –Cr	5276·17 5276·24	— —	3 6	3 2	5276·16	4	
5280·81	1	0	—	—	—	—	—	5281·39	1	
5284·66	2	2	—	—	—	—	—	5283·92	2	
5289·46	1	0	—	—	—	—	—	—	—	
5293·82	1	1	—	—	—	—	—	—	—	
5299·00	1	0	—	—	—	—	—	5297·97	1	
5302·97	1	1	Fe	5302·48	—	10	5	5302·38	1	
5312·53	1	0	—	—	—	—	—	—	—	
5316·94	2	4	Fe	5316·79 5316·96	3 —	2 —	4 2	5316·88	4	Enh. sp. 3. Arc 0. Lockyer.
5329·03	2	2	—	—	—	—	—	5328·33	4	
5337·39	2	1	Ti	5336·97	—	3	4	5336·84	1	
5341·05	1	0	Fe	5341·21	—	8	7	5340·95	1	
5362·83	2	1	—	—	—	—	—	5262·92	2	
5371·72	2	2	Cr Fe	5371·66 5371·73	— —	0 10	2 3	5371·58	3	
5377·65	1	0	—	—	—	—	—	—	—	
5381·18	1	0	—	—	—	—	—	5381·00	1	

Spectrum of chromosphere.			Probable identification.					Lord.	
Wave-length.	No. of photos.	Intensity.	Element.	Wave-length.	Intensity.			Wave-length.	Intensity.
					Spark.	Arc.	Sun.		
5404·65	1	0	Fe	5404·36	—	8	5	5404·25	1
5406·37	2	1	Fe	5405·99	—	10	6	5405·79	2
5410·65	2	1	—	—	—	—	—	5410·02	1
5415·12	2	1	Fe	5415·42	—	10	5	5415·03	1
5419·63	1	0	—	—	—	—	—	5419·12	1
5425·49	2	2	—	5425·47	—	—	1	5425·06	1
5430·00	2	2	Fe	5429·91	—	10	6d ?	5429·65	2
5434·58	2	1	Fe	5434·70	—	8	5	5434·69	2
5447·19	2	2	Fe	5447·13	—	10	6d ?	5447·08	2
5451·94	2	1	—	—	—	—	—	—	—
5456·36	2	2	Fe	5455·83	—	10	4	5455·86	3
5463·35	2	2	Fe	5463·17	—	1	3	5462·70	1
				5463·49	—	8	3		
5466·83	2	1	Fe	5466·61	—	4	3	—	—
5473·43	2	1	—	—	—	—	—	—	—
5477·21	2	3	—	—	—	—	—	5476·86	2
5482·52	2	1	—	—	—	—	—	—	—
5488·31	1	0	—	—	—	—	—	—	—
5493·41	1	0	—	—	—	—	—	—	—
5498·16	1	0	Fe	5497·74	—	1	5	5497·73	1
5503·08	1	0	Fe	5501·68	—	8	5	5501·62	1
5507·14	1	0	Fe	5507·00	—	8	5	5506·69	1
5510·85	1	0	—	—	—	—	—	—	—
5514·15	1	1	—	—	—	—	—	—	—
5527·23	2	3	Sc	5527·03	—	—	3	5527·65	2
5535·37	2	3	—	—	—	—	—	5535·30	2
5540·96	1	0	—	—	—	—	—	—	—
5544·92	2	2	—	—	—	—	—	—	—
5555·39	1	0	Fe	5555·12	—	6	3	—	—
5588·23	1	0	—	—	—	—	—	5588·09	1
5600·15	1	0	—	—	—	—	—	—	—
5602·73	1	2	—	—	—	—	—	5602·57	1
5615·59	1	2	Fe	5615·88	—	10	6	5615·52	1
5616·95	1	1	—	—	—	—	—	—	—
5619·97	1	1	—	—	—	—	—	—	—
5623·40	1	0	—	—	—	—	—	—	—
5625·33	1	2	Fe	5624·77	—	8	4	5624·98	1
5635·16	1	1	—	—	—	—	—	—	—
5642·52	2	1	—	—	—	—	—	5641·17	1
5647·57	1	0	—	—	—	—	—	—	—
5658·42	2	2	Y	5658·10	—	—	2	5658·02	1
5663·17	1	1	Y	5663·15	—	—	1	5663·56	1
5668·02	1	1	—	—	—	—	—	—	—
5875·87	2	3	He	5875·87	10	—	—	—	—

Hydrogen.

In the following table a comparison is given of the measured wave-lengths of the hydrogen lines with those computed by the formula

$$\lambda = \frac{1}{a}\cdot\frac{n^2}{n^2-4}\left[\text{where } a = \frac{1}{27418{\cdot}75} \text{ and is derived from \textsc{Rowland}'s values for } H_\alpha, H_\beta, H_\gamma\right]$$

and corrected for air :—

Line.	Intensity.	Wave-length.	Tabular.	T − O.	
δ	30	4101·92	1·90	−0·02	
ϵ	30	3970·21	0·22	+0·01	
ζ	20	3889·15	9·20	+0·05	He line at 3888·72.
η	20	3835·53	5·53	0·00	
θ	19	3798·06	8·04	−0·02	
ι	15	3770·79	0·77	−0·02	
κ	10	3750·32	0·30	−0·02	
λ	12	3734·52	4·51	−0·01	
μ	12	3722·05	2·08	+0·03	
ν	10	3712·12	2·11	−0·01	
ξ	10	3704·00	4·00	0·00	
o	8	3697·29	7·29	0·00	
π	8	3691·70	1·70	0·00	
ρ	7	3687·00	6·97	−0·03	
σ	4	3682·92	2·95	+0·03	
τ	3	3679·50	9·49	−0·01	
υ	3	3676·54	6·50	−0·04	
ϕ	3	3673·90	3·90	0·00	
χ	3	3671·46	1·48	+0·02	Zr line at 3671·41.
ψ	2	3669·58	9·60	+0·02	
ω	2	3667·89	7·82	−0·07	
α'	2	3666·21	6·24	+0·03	
β'	3	3664·78	4·82	+0·04	Y line at 3664·76.
γ'	2	3663·58	3·54	−0·04	
δ'	2	3662·35	2·40	+0·05	Ti line at 3662·38.
ϵ'	1	3661·39	1·35	−0·04	

The agreement with the formula is very close: there is a mean difference of −·010 which could be corrected by a slight change in the constant, but it is open to doubt whether this is a real difference. It seems that BALMER'S law for the hydrogen lines holds to within about ·01 of a tenth-metre.

Helium.

The helium lines are strongly shown, but those of par-helium are doubtful. There is a line at 4388·10 which may coincide with 4388·15, intensity 3. The line at 3964 possibly occurs as a compound line. The lines at 5015 and 4922 are not shown.

Argon, Xenon, Neon, Krypton.

There is no evidence of the presence of these gases in the chromosphere.

Carbon.

A number of carbon lines including the heads of the band at 3833 are shown, but not very strongly.

Sodium.

The lines D_1 and D_2 can be seen faintly on one of the Sumatra photographs, and the lines at 3303 are probably shown.

Magnesium.

The *b* lines and the triplet at 3838, 3832, 3829 are very strongly shown, but that at 3336, 3332, 3329 is not shown. The arc lines at 4352 and 4703 may possibly be represented in compound lines. The strongly enhanced line at 4481·3 may possibly be shown by a line of intensity 1, but the latter line measured can be satisfactorily identified with a titanium line.

Aluminium.

The strong arc lines at 3944 and 3961 are shown fairly strongly. The three strong spark lines at 3581·02, 3601·95, and 3612·68 are possibly faintly shown; but the line at 3587·15, intensity 0, may well be due to Fe, and the line at 3602·05 is easily accounted for as Y. There still remains a line 3612·65, intensity 0, which may be the Al line.

Silicon.

The following table gives a detailed comparison of all the lines in Exner and Haschek's list with the lines in the chromosphere which are possibly coincident with them :—

Spark lines (Exner and Haschek).		Chromosphere.			
Wave-length.	Intensity.	Wave-length.	No. of photos.	Intensity.	
3796·50	2	3796·44	1	1	
3806·90	3	Not shown			
3853·62	1	3853·61	1	1	Possibly C.
3854·02	1	Not shown			
3856·19	6	3855·87	1	1	C. at 3855·77, intensity 3 in sun.
3862·80	4	3862·79	4	2	
3883·46	1	3883·38	3	3	Coincides with head of first C. band.
3905·71	5	3905·68	4	0	In ⊙ 3905·66 Si, 12. Chrom. line possibly enh. Cr.
4021·0	1	Not shown			
4030·1	2	4029·95	4	1	
4096·8	1	4097·05	1	0	
4103·2	1	4103·15	1	2	In ⊙ 4103·10 Si, Mn 5. Probably not Mn in chrom.
4128·208*	5	4128·31	4	2	Possibly 4128·25 V.
4131·040*	6	4130·96	6	2*	Possibly 4130·88 Ba.
4552·7	3	4552·64	2	0	
4567·95	1	Not shown			
4574·9	1	4574·95	1	1	
4764·20	2	4764·39	1	2	Possibly enh. Ti 4764·11.

* Wave-lengths determined by Hartmann.

A good deal of caution is necessary in establishing the identical origin of the weak lines, but the cumulative evidence of the close agreement of the wave-lengths of the lines 3862, 3905, 4103, 4128, 4131, and 4552 gives a fair degree of probability for the existence of Si in the chromosphere.

Calcium.

The calcium lines are very strongly shown, and the intensities follow closely those given by Exner and Haschek for the spark spectrum.

Chromosphere.			Intensity in—		Chromosphere.			Intensity in—	
Wave-length.	No. of photos.	Intensity.	Spark.	Arc (K. and R.).	Wave-length.	No. of photos.	Intensity.	Spark.	Arc (K. and R.).
3706·18	11	5*	10	4	4302·68	2	1 ?	6	10
3737·08	11	8*	15	4	4307·92	4	4*	2	8
3933·84	13	100	100	10	4318·79	—	—	3	8
3968·63	13	80	80	10	4425·62	—	—	3	10
4226·91	4	5	10	10	4435·12	2	2	4	10
					4435·84			3	8
					4454·93	2	1	5	10

* Compound lines.

Comparison of the two sides of the above table shows the relative behaviour of enhanced and unenhanced lines, the 7 strong arc lines on the right being only just shown, if at all, in the chromosphere spectrum.

Scandium.

Scandium is very strong in the chromospheric spectrum. Exner and Haschek give 23 lines of intensity 10 or greater. The only one of these not found in the chromospheric spectrum is 3558·72, intensity 20. The intensities agree well with the spark. All the lines are present in the solar spectrum.

Titanium.

Titanium is very strong in the chromospheric spectrum. Analysing the results, taking Exner and Haschek's spark spectrum as argument, it is found that: (i) The 7 lines of intensity 50 are all strongly shown. These are all fairly strong arc lines, but two of them, 3383·91 and 3505·06, are weak in the solar spectrum. (ii) The 5 lines of intensity 30 are well shown. They are all strong in the solar spectrum. The lines 3741 and 3913 are decidedly "enhanced." (iii) Of the lines of intensity 20 the weakest in the chromosphere is 3989·91, a line strong in the arc and the sun. (iv) The lines of intensity 15 are strongly shown, with three exceptions, viz.—3653·64 and 3998·79 very strong in the arc and strong in the sun, and 3456·53 of intensity 3 in the sun and outside the limit of Hasselberg's arc spectrum. (v) The lines of intensity 10, 9, 8 and 7 are generally well shown, except at the red end of the spectrum. The strongest lines in the chromosphere are "enhanced," *e.g.*, 4012·54, 3757·82, 4172·07. The lines 3753·00, 3924·67, 3948·82, 3956·48 may be instanced as lines strong in the arc and the sun, but missing in the chromosphere.

The behaviour of the titanium lines may be instanced from almost any part of the spectrum. A good variety of lines is shown between 3900 and 3950.

Wave-length.	Chromosphere.	Spark.	Arc.	Sun.
3900·68	7	50	2·3	5
3904·93	—	10	3·4	3
3913·61	7	30	2·3	5
3924·67	—	7	2·3	4
3932·16	3	6	—	1
3947·92	0	9	3·0	2

Vanadium.

Vanadium is not at all strong in the chromosphere. The strongest arc lines, 4379 and 4384, are not shown. There is, however, reason to think some of the "enhanced" lines are present, as will be seen from the following table:—

Chromosphere.			Solar spectrum.		Spark* intensity.	Arc* intensity.	
Wave-length.	No. of photos.	Intensity.	Wave-length.	Intensity.			
3517·51	3	1	3517·45	– V 3	20	4	
3520·21	1	0	3520·17	2	14	4	
3530·90	4	2	3530·92	3	20	4	
3545·27	3	1	3545·34	– V 4	20	4	
3566·21	3	1	3566·11 3566·31	Ti 1 – 2N	12	3	
3592·16	7	3	3592·17	V ? 2	18	4	
3700·41	2	1	3700·48	1	12	—	
3715·60	8	3	3715·62	Mn ? 4	20	4	
3718·44	2	1	—	—	10	—	Wave-length 3718·35 in spark.
3727·46	2	1	3727·49	1	16	4	
3728·49	2	1	—	—	10	—	„ 3728·51 „
3736·11	3	1	—	—	10	—	„ 3736·16 „
3771·06	1	0	3771·12	2	20	4	
3787·34	1	1	—	—	16	2	„ 3787·39 „
4023·55	6	2	4023·53	V-Co 3	20	4	
4090·78	3	2	4090·73	V ? 1	16	6	
4095·58	1	0	4095·63	V 0	12	6	
4116·66	1	1	4116·63 4116·71	V 1 V, Fe ? 0	14	6 3	

* From 'WATTS' Index,' Appendix M.

It should at the same time be noted that a number of enhanced lines are not seen, but this may be expected when the lines which are shown are all weak.

Chromium.

Chromium is very strong in the chromospheric spectrum. The only strong spark line in EXNER and HASCHEK's list which is missing is 3976·82 of intensity 9. Strong arc lines are shown, but it is the enhanced lines which are strongest. In the following table the intensities in the sun, spark, and arc, are taken from Mr. JEWELL's paper :—

Enhanced lines					Strong arc lines.				
Wave-length.	Chromo-sphere.	Sun.	Spark.	Arc.	Wave-length.	Chromo-sphere.	Sun.	Spark.	Arc.
3408	4	3	20	3	3578	1	10	20	30
3421	4	4	10	3	3593	2	9	10	30
3422	4	4	10	4	3605	1	7	20	20
3433	5	3	10	3	4254	3	8	50	50
3603	2	3	10	0	4274	3	7	30	50

Manganese.

Manganese is not so strong as chromium, and only some of the strongest spark lines of EXNER and HASCHEK's list are shown. Some strong arc lines from 4754 to 4823 are feebly shown, the strongest arc lines near 4030 are well shown. The strongest chromospheric lines are given below.

Enhanced lines.					Strongest arc lines.				
Wave-length.	Chromo-sphere.	Sun.	Spark.	Arc.	Wave-length.	Chromo-sphere.	Sun.	Spark.	Arc.
3442	4	6	40	7	4030	2	12	20	30
3460	3	4	40	3	4033	1	10	20	25
3474	2	4	40	—	4034	1	8	10	20
3483	2	5	30	3					
3488	2	4	30	3					

Iron.

The following table gives some of the stronger iron lines from 3735 to 3930. Lines are avoided whose origin either in the sun or chromosphere is ambiguous. The intensities of the arc lines are taken from KAYSER and RUNGE's list :—

Wave-length.	Intensity in the—				Wave-length.	Intensity in the—			
	Chromo-sphere.	Sun.	Spark.	Arc.		Chromo-sphere.	Sun.	Spark.	Arc.
3733	4	7	10	8	3816	6	15	9	8
3738	3	3	3	6	3824	7	6	7	8
3745	10	{ 8	7	8	3826	8	20	9	8
		6	7	6	3828	7	8	9	8
3748	7	10	7	6	3834	8	10	8	8
3749	4	20	8	10	3856	4	8	8	8
3758	4	15	8	8	3860	5	20	9	10
3763	7	10	7	8	3873	4	7	8	8
3765	3	6	5	8	3886	4	15	8	6
3767	6	8	7	8	3895	3	7	5	6
3788	3	9	5	6	3899	3	8	6	6
3790	3	5	3	6	3923	2	12	6	8
3795	3	8	8	6	3928	4	8	7	8
3799	4	7	7	6	3930	4	8	6	8

The intensities of the lines in the chromosphere on the whole follow the spark spectrum most nearly. It may be noticed, too, that the lines which are specially strong in the sun (compare, *e.g.*, 3826 and 3828) are not specially strong in the chromosphere, spark, or arc.

The most striking enhanced lines are not in this part of the spectrum. The following list gives some of those which are very faint in the spark with a comparison with neighbouring arc lines :—

Enhanced lines.					Arc lines.				
Wave-length.	Intensity in the—				Wave-length.	Intensity in the—			
	Chromo-sphere.	Sun.	Spark.	Arc.		Chromo-sphere.	Sun.	Spark.	Arc.
4385	4	2	1	—	4383	5	15	10	10
4489	3	2	1	—	4405	1	10	10	10
4491	3	2	1	—	4415	1	8	10	8
4508	3	4	2	1	4482	1	5	4	8
4515	3	3	1	1	4528	1	8	6	10
4520	4	3	1	1					
4522	5	3	2	1					
4556	4	3	1	1					

Nickel.

Nickel is very weak in the chromospheric spectrum. About a dozen lines can with considerable probability be attributed to it. These are the strongest spark lines of

Exner and Haschek, and are generally strong in the arc and the sun. Enhanced lines are possibly shown at 4067 and 4245, but the identification is not certain. The line at 3769 may well be enhanced Ni.

Chromosphere.			Wave-length.	Sun.	Spark.	Arc.
Wave-length.	No. of photos.	Intensity.				
3769·66	4	3	3769·60	3	20	1

A considerably enhanced line at 3484 is not shown.

Cobalt.

Cobalt, like nickel, is very weak. There are enough lines to assert its existence in the chromosphere with certainty. They are all of intensity 1 or 0, with the exception of an enhanced line at 3621. There are 16 arc lines of intensity 9 or 10 given by Hasselberg, and 3502·4 and 4118·9 are the only ones certainly not shown.

Chromosphere.			Wave-length.	Sun.	Spark.	Arc.
Wave-length.	No. of photos.	Intensity.				
3621·38	3	2	3621·34	2	10	—

Zinc.

The strong arc triplet, 4680, 4722, 4810, is possibly shown, though faintly, in the chromospheric spectrum.

Chromosphere.		Wave-length.	Sun.	Arc.
Wave-length.	Intensity.			
4680·26	1	4680·32	Zn 1	20
4722·49	2	4722·34	Zn 3	20
4811·04	2	4810·72	Zn 3	20

Mr. Lord gives lines at 4722·23 and 4810·90 of intensity 1. The line at 3345·4 is not shown, and it is impossible to say whether 3302·90 is shown owing to the proximity of Na.

Strontium.

Two of the strongest lines in the chromosphere are due to Sr. These are strong arc lines and extremely strong in the spark. Two other lines, almost equally strong in the spark and arc, are not shown.

Wave-length.	Spark.	Arc.	Chromosphere.	Sun.
3380·89	80	8	—	Sr ? 1
3464·58	100	8	—	1
4077·88	100	10	15	Sr 8
4215·66	100	10	12	Sr 5d ?

Possibly a line at 4305·61 is also shown.

Yttrium.

Yttrium is strongly shown, all the strong spark lines of Exner and Haschek being present. At least 20 lines may be safely identified as yttrium.

Zirconium.

A few of the stronger arc lines given by Rowland and Harrison occur in the chromosphere, while practically all the strong spark lines given by Exner and Haschek are shown. As this element furnishes a good illustration of the relationship of the chromospheric and solar spectra to those of the spark and arc, the lines assigned to zirconium in the chromosphere are given below.

Wave-length.	Intensity in the—				Wave-length.	Intensity in the—			
	Chromosphere.	Sun.	Spark.	Arc.		Chromosphere.	Sun.	Spark.	Arc.
3392·11	1	2	15	10	3668·61	0	00	4	—
3404·95	1	0	6	5	3674·85	2	1	10	3
3410·39	2	1	8	1	3698·28	3	2*	10	—
3430·71	1	1	10	3	3714·92	2	0	6	—
3438·38	2	2	15	5	3731·37	2	0*	10	—
3479·48	1	2	10	—	3751·80	2	00	12	—
3481·31	2	2*	10	5	3766·94	2	1*	10	—
3496·33	2	2	20	7	3836·91	4	1*	12	—
3505·77	1	1*	8	4	3914·58	2	1	4	—
3552·11	2	1	10	3	4048·82	2	1	10	7
3556·81	3	2	15	5	4149·33	3	2	20	10
3577·00	2	1	10	—	4209·15	2	1	10	—
3614·92	3	2	10	5	4258·24	2	0	5	7
3624·03	1	1	8	4	4348·06	1	1	8	3
3630·13	1	1	5	1	4379·94	2	0	12	7
3636·69	0	1	4	1	4403·49	2	0	4	1

* Compound lines.

The arc spectrum with which comparison was made contains 250 lines, including 8 of intensity 10 and about 30 of intensity 7 or 8. Yet of the 32 lines given above, 11 are not found in the arc spectrum and 4 are of intensity 1, while only 6 can be called strong arc lines.

The line 3542·77, of intensity 12 in the spark and absent in the arc, and of intensity 00 in the sun, is an exceptional case where an enhanced line does not appear in the chromosphere.

Barium.

The arc lines at 4554 and 4934 are strongly shown, and probably the line at 5535·37, intensity 2, is the Barium line 5535·69. None of the enhanced lines are shown.

Lanthanum.

A number of strong arc lines are shown. These lines are all strong in the spark except (if due to La) 4105·07, which is of intensity 1 in the spark and 10 in the arc. But as there is an unidentified solar line at 4105·10 and the La arc line is given by Rowland as 4105·03, it is possible that these lines are not identical, and that the chromospheric line agrees with the former. Enhanced lines at 3737·67 and 3871·89 are not shown, but 3517, 3713, 3790, 3949, 4196 are shown.

Cerium.

The spark spectrum of cerium has no very strong lines. Ten of intensity 10, 9, or 8 are given by Exner and Haschek in the region considered, but the places of two are occupied by enhanced Ti and Fe lines. The remaining 8 are as follows:—

Spark.		Chromosphere.			Sun.	
Wave-length.	Intensity.	Wave-length.	No. of photos.	Intensity.	Wave-length.	Intensity.
3801·71	8	3801·62	7	3	3801·68	– C 0 Nd ?
4133·98	10	4133·83	4	1	4133·97	Ce 0
4137·78	9	4137·54	7	3	4137·57	2
4150·09	10	4150·10	4	2	4150·06	Ce 00
4152·13	9	4152·14	5	2	4152·11	Fe-La 2
4165·75	10	4165·71	3	2	4165·76	Ce – 2
4186·71	10	4186·76	1	1	4186·78	Ce-Zr, 2N
4360·38	8	—	—	—	—	—

The line 4137 is probably the solar line 4137·57, but not cerium; cerium may have contributed to the lines at 4152 and 4186. The other lines are probably due to cerium, though the line 4133 is somewhat doubtful. The conclusion, slightly strengthened by the lines of intensity 5, 6, 7 in the spark, is that cerium is present, but very weak, in the chromospheric spectrum.

Præsodymium.

Some strong spark lines appear to be shown, but an equal number not.

Neodymium.

There seem to be a large number of lines which can be identified with this element. Few of them are very strong, and there is frequently doubt about the identifications. The following lines are, however, probably due to neodymium :—

Chromosphere.			Wave-length.	Sun.	Spark.
Wave-length.	No. of photos.	Intensity.			
3906·03	2	0	3906·04	Nd −3	4
3911·29	2	0	3911·32	Nd 0	7
3994·87	3	2	3994·83	Nd 2	5
4061·28	5	1	4061·24	Nd 3	10
4109·61	6	4	4109·61	Nd? 1	8

Samarium.

Possibly some of the strongest spark lines are shown.

Gadolinium.

There is a strong line at 3768·46 in the chromosphere which has been attributed with some hesitation to the strongest line in the spectrum of gadolinium.

Chromosphere.			Wave-length.	Sun.	Arc.	Spark.
Wave-length.	No. of photos.	Intensity.				
3768·46	6	3	3768·54	Gd ? 0	20	20

Several of the strong lines are possibly shown, but two of intensity 12 at 3422 and 3719 are missing.

Ytterbium.

The very strong spark line at 3694·35 is shown. The next strongest spark line is also seen.

Chromosphere.			Wave-length.	Sun.	Spark.	Arc.
Wave-length.	No. of photos.	Intensity.				
3479·02	1	0	3479·05	000	20	—
3694·29	8	4	3694·34	Yb 3	200	10

Tantalum.

The strongest spark lines are possibly shown.

Lead.

The strongest arc lines appear to be faintly shown, but not the enhanced lines. The following table gives all the strongest lines in Exner and Haschek :—

Spark.		Chromosphere.			Wave-length.	Sun.	Arc.
Wave-length.	Intensity.	Wave-length.	No. of photos.	Intensity.			
3572·95	20	3573·19	1	0 ?	—	—	8r
3639·72	20	3639·66	1	1	3639·66	Pb 1	10r
3683·60	20	3683·70	3	0	3683·62	Pb 000	10r
—	—	—	—	—	3683·76	Fe 2	—
3740·10	20	3740·19	2	0	—	—	8r
3786·37	20	3786·29	1	1	3786·31	Fe 4d ?	—
3854·05	20	Not shown					
4058·05	20	4058·02	2	1	4058·04	Pb 0	10r
4245·2	20	Not shown					
4387·0	20	4387·01	2	1	4387·01	Ti ? 1	—

The evidence, such as it is, is in favour of the presence in the chromosphere of the three lines of intensity 10 in the arc, though the line at 4058·05 may just as well be a spark line of tantalum.

Europium.

'Watts' Dictionary of Spectra' (Appendix M.) gives the intensities in the spark and arc of the strongest lines.

Wave-length.	Intensity.		Chromosphere.			
	Spark.	Arc.	Wave-length.	No. of photos.	Intensity.	
4662·1	50	5	4662·32	1	0	
4627·4	100	8	—	—	—	
4522·8	20	15	4522·80	5	5	Enh. Fe.
4435·7	50	30	4435·53	2	2	
4205·2	100	50	4205·21	5	4	
4129·9	100	100	4129·87	5	4	In sun 29·88, intensity 1.
3972·2	50	50	3972·02	5	2	In sun 72·13, intensity 0 ?
3930·7	50	50	3930·46	5	4	Fe.
3907·3	30	30	3907·28	6	2	
3819·8	50	50	3819·73	3	1	He.
3725·1	30	20	3724·97	3	1	
3688·6	20	10	—	—	—	

The strongest spark lines, 4205·2 and 4129·9, are strongly shown.

Aluminium, magnesium, barium, zinc and lead appear to show the arc lines, but not the enhanced lines, or at most very faintly. They are exceptions to the very general rule, and the important part the enhanced lines and strong spark lines take in the chromospheric spectrum is amply demonstrated for the different metals discussed wherever it has been possible to compare with both an arc and spark spectrum, particularly for titanium, iron, chromium, scandium, yttrium and zirconium.

The extent of spectrum considered and the accuracy with which the wave-lengths have been determined makes the identification of nearly all the brighter lines tolerably certain. I have compared the results with those obtained by Sir N. LOCKYER, Mr. EVERSHED, Professor FROST, Professor LORD, Dr. HUMPHREYS, Dr. MITCHELL and Dr. JEWELL, and have without scruple availed myself of their opinions of the identification of lines which I might otherwise have overlooked. The method of identification of lines pursued has been, generally speaking, by comparison with the strongest spark lines given by EXNER and HASCHEK. When the enhanced lines as given in Sir N. LOCKYER'S identification of the chromospheric spectrum obtained in the 1898 eclipse are added, the principal lines are well accounted for.

Spectrum of the Higher Chromosphere.

At the eclipse of 1905, August 30, the photographs taken for the spectrum of the corona contain a number of chromospheric lines. The slit of the spectroscope which was set nearly tangential to the sun passed through the large prominence which was near the point of second contact.

The following table gives the observed wave-lengths determined by means of HARTMANN'S formula. One photograph extends from 4026 to 4501, and the other from 4685 to 5875. It will be seen that the helium lines and the line 4685·86 are stronger in the higher than the lower chromosphere. The enhanced iron lines appear to be weakened in the higher chromosphere in comparison with the Mg arc lines and the enhanced titanium lines.

SPECTRUM of the Higher Chromosphere.

Observed wave-length.	Identification.		Intensity.	Intensity in lower chromosphere.	
4026·20	4026·34	He	6	?	+
4077·84	4077·89	Sr	8	15	
4101·88	4101·91	H	20	60	
4120·95	4120·97	He	1	?	+
4215·71	4215·70	Sr	8	12	
4226·93	4226·90	Ca	4	6	
4233·47	4233·33	Fe	2	7	– Enh. Fe.
4247·00	4247·00	Sc	6	10	
4254·50	4254·51	Cr	2	3	
4272·09	4271·93	Fe	1	2	
4274·93	4274·96	Cr	1	3	
4290·25	4290·37	Ti	2	5	Enh. Ti.
4294·26	4294·27	Ti and Fe	2	2	
4300·21	4300·20	Ti	4	5	Enh. Ti.
4308·11	4308·08	Fe	2	4	
4312·81	4313·02	Ti	1	3	Enh. Ti.
4315·29	4315·14	Ti	1	3	Enh. Ti.
4320·92	4320·91	Sc	2	4	
4325·98	4325·94	Fe	2	4	
4338·06	4338·08	Ti	2	5	Enh. Ti.
4340·64	4340·63	H	30	100	
4351·75	4351·93	Fe, Cr	1	4	– Enh. Fe.
4383·63	4383·72	Fe	4	5	
4387·98	4388·10	He	4	1	+
4395·14	4395·20	Ti	8	8	Enh. Ti.
4404·79	4404·89	Fe	3	1	+
4415·69	4415·72	Sc	1	2	
4417·89	4417·88	Ti	2	3	Enh. Ti.
4420·37	—	—	1	—	+
4443·93	4443·98	Ti	4	6	Enh. Ti.
4468·67	4468·66	Ti	4	5	Enh. Ti.
4471·64	4471·65	He	20	7	+
4501·39	4501·44	Ti	4	6	Enh. Ti.
4685·86	—	—	2	—	+
4713·29	4713·25	He	6	1	+
4861·53	4861·53	H	40	100	
4921·92	4922·10	Parh	2	?	+
4924·03	4924·11	Fe	2	8	– Enh. Fe.
5015·69	5015·73	Parh	2	—	+
5018·85	5018·63	Fe	1	7	– Enh. Fe.
5167·53	5167·50	Mg	1	0	
5169·48	5169·22	Fe	1	4	– Enh. Fe.
5172·88	5172·86	Mg	4	4	
5183·79	5183·79	Mg	6	5	
5875·87	5875·87	He	20	3	+

Spectrum of the Corona.

The following are the wave-lengths determined at the three eclipses of 1900, 1901, and 1905 :—

1900.	1901.	1905.	Mean.	Intensity.
—	—	5535·8	5535·8	2
—	5304	5303·1	5303·1	20
—	—	5117·7	5117·7	2
5073	—	—	5073	1
4779	—	—	4779	1
4725 ?	—	—	4725	—
4722 ?	—	—	4722	—
4586·3	—	—	4586	4
4566·5	4565	—	4566	6
4400	—	—	4400	1
4358·8	—	—	4359	4
4311·3	—	—	4311	2
4230·6	4230·9	4231·1	4231·0	5
4130	—	—	4130	—
—	—	4087·4	4087	—
3987·2	3987	3987·1	3987·1	3
—	3891·2	—	3891	—
3800·8	3801·1	3800·8	3800·9	3
3642·9	—	3642·0	3642·5	2
—	3505 ?	—	3505 ?	—
3461·3	—	—	3461	1
—	3454	—	3454	9
—	3387·9	—	3387·9	12
—	3361 ?	—	3361 ?	—

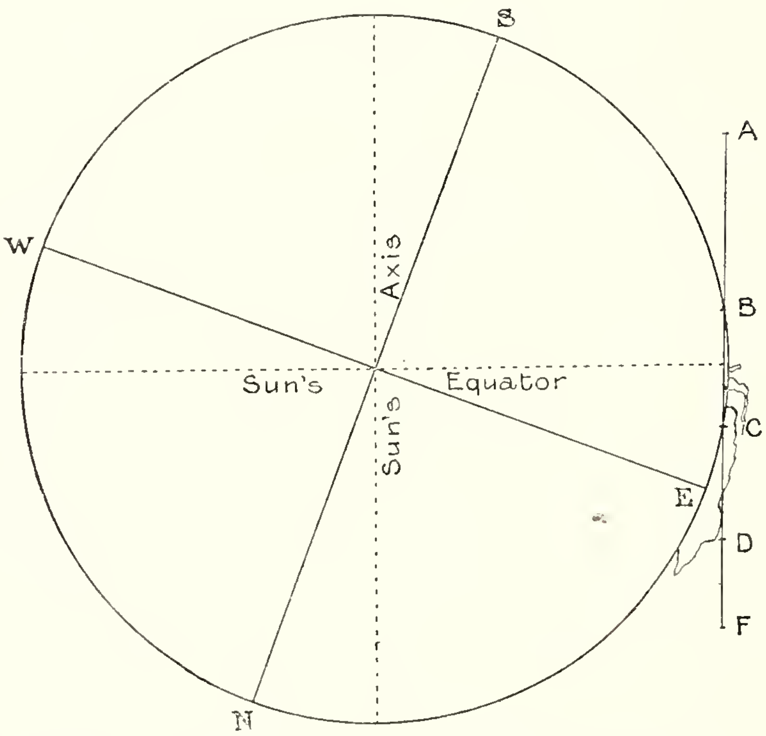
The photographs taken in 1905 are in excellent definition in the green and at the line 4231. The part from 4500 to 4685 is, unfortunately, not given, as the plates were carried back from Sfax separated by thin pieces of card and fogged where these were in contact. The lines in the extreme ultra-violet were only obtained in Sumatra. The wave-lengths were determined by reference to chromospheric lines by means of HARTMANN'S formula.

Experience gained in these three eclipses shows that a slit spectroscope is most advantageously used when tangential as nearly as possible to the sun at the point of second contact. This applies both to the chromospheric and the corona spectrum.

DESCRIPTION OF PLATE 9.

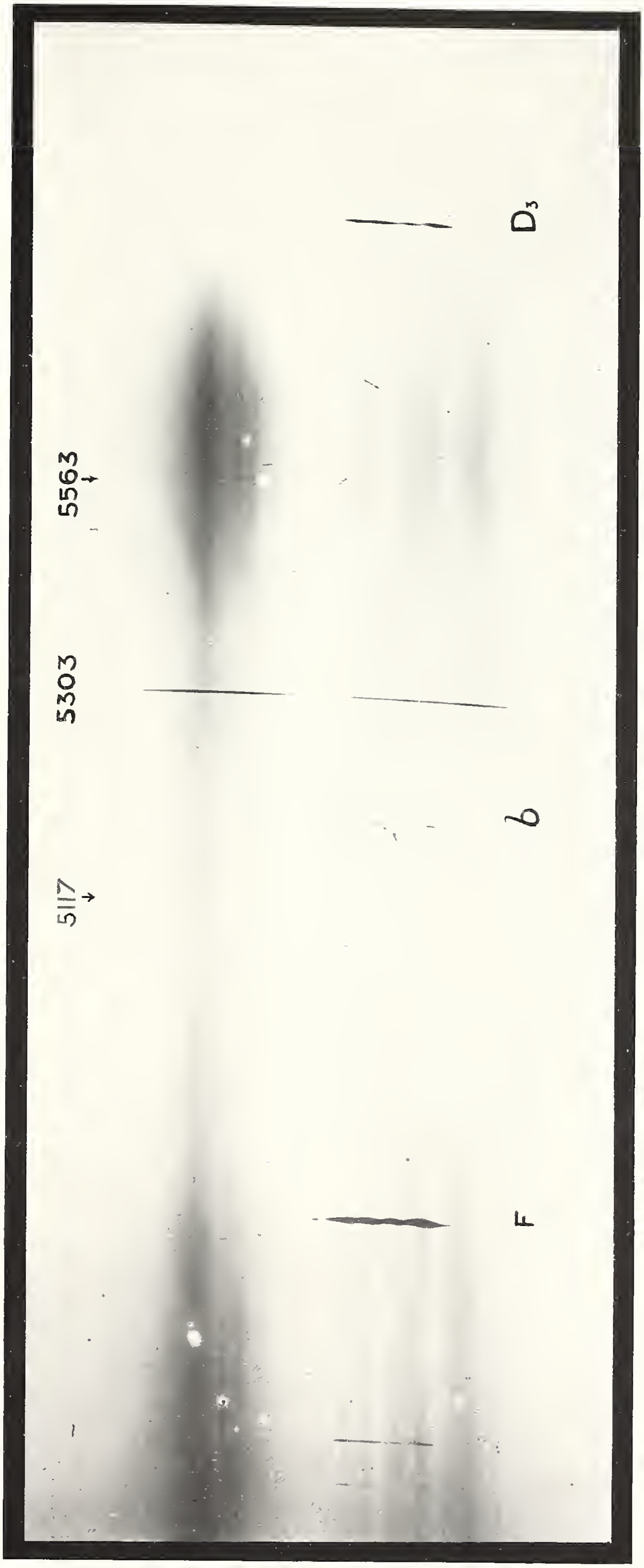
SPECTRUM OF THE CORONA AND HIGHER CHROMOSPHERE, OBTAINED AT SFAX AT THE TOTAL ECLIPSE OF 1905, AUGUST 30.

The photograph was exposed from about 15 seconds after the beginning of totality to about 15 seconds from the end, the slit being nearly tangential to the sun at the point of second contact and passing through a large prominence. The plate is made from a copy on glass (enlarged about four times) of the original negative. The two corona lines at 5117 and 5563 have been slightly accentuated to make them clearly visible on the plate.



In the above diagram, which is drawn to scale, the line ABCDF gives the breadth of the spectrum obtained. The continuous spectrum is shown corresponding to AB and CF, but is strongest in the part AB, which shows two faint lines at 5563 and 5117. The chromospheric lines are shown in the part corresponding to CD and end sharply. No chromospheric lines are seen in the part AB.

7 SEP.


D₃
5563
5303
b
5117
F

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[PLATES 10–19.]

RESEARCHES ON EXPLOSIVES—PART IV.

BY

SIR ANDREW NOBLE, BART., K.C.B., D.Sc. (OXON.), D.C.L., F.R.S.

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IX. *Researches on Explosives.—Part IV.*[*]

By Sir Andrew Noble, *Bart., K.C.B., D.Sc. (Oxon.), D.C.L., F.R.S.*

Received June 28,—Read June 28, 1906.

[Plates 10–19.]

In Part III. of my 'Researches on Explosives' I gave the results of a very extensive series of experiments, the completion of which necessarily occupied a very long time, and the particular explosives with which I experimented were those with which artillerists in this country were familiar, and with which a considerable number of experiments had been made.

These explosives were (1) the cordite of the service known as Mark I; (2) the modified cordite known as M.D.; and (3) the nitrocellulose known as Rottweil R. R.

The experiments made by myself extended, for all the above explosives, from densities of 0·05 to 0·45 or 0·50, and pressures of from 2·75 tons per sq. inch (419 atmospheres) to pressures of 60 tons per sq. inch (9145 atmospheres), and although the transformation on ignition varied both with regard to the particular explosive employed and for each explosive as regards the density at which it was fired, yet when the observations were represented by curves drawn through or near the observed points there was a pretty close resemblance in the form of the curves, not only in respect to the variations in the quantities of the gases generated at the varied densities, but also with regard to the units of heat developed and the volumes of gas produced.

Certain anomalies, chiefly with reference to the temperature of explosion at different densities, having appeared, I was anxious to make experiments with other explosives, and I have accordingly completed a similar examination of three other explosives, and the composition of the six explosives was approximately as follows :—

---

[*] Small alterations are required in some of the figures given at the higher densities, owing to experiments which have been carried out at a density of 0·50 since the paper was prepared. The curves, however, have all been corrected to the later results.

I.		II.	
Mark I cordite.	Percentage.	M.D. cordite.	Percentage.
Nitroglycerine	58·0	Nitroglycerine	30·0
Nitrocellulose	37·0	Nitrocellulose	65·0
Mineral jelly	5·0	Mineral jelly	5·0
III.		IV.	
Norwegian 165.	Percentage.	Norwegian 167.	Percentage.
Nitroglycerine	36·0	Nitroglycerine	40·0
Nitrocellulose	52·0	Nitrocellulose	50·0
Nitronaphthalene	6·0	Nitronaphthalene	5·0
Secret ingredient	6·0	Secret ingredient	5·0
V.		VI.	
Italian.	Percentage.	Nitrocellulose.	Percentage.
Nitroglycerine	47·1	Nitrocellulose (sol.)	85·5
Nitrocellulose (sol.)	52·3	Nitrocellulose (insol.)	14·5
Nitrocellulose (insol.).	0·6		

The results of my experiments with Explosives I., II. and VI. have been given in my ‘Researches on Explosives,’ Part III.,[*] and if reference be made to Plates 8, 9 and 10 in that paper, it will be seen how well, on the whole, the curves, showing the variation in the percentages of the gases, represent the observations. Similar curves, representing very accurately the observations, are now given for Explosives III., IV. and V. Some doubt might, however, be felt as to whether the transformation of the same explosive at the same density might be relied upon as being practically identical, and to test this point the following experiments were made :—

In Experiment 1586, a charge of Explosive III. at a density of 0·4 and pressure of 37·92 tons per sq. inch (5780 atmospheres) was fired, and analysis gave the percentage volumes of the permanent gases as follows :—

---

[*] ‘Phil. Trans.,’ A, vol. 205, pp. 221, 222 and 223.

	Experiment 1586.	Experiment 1593.
	per cent.	per cent.
CO_2	33·10	33·00
CO	28·70	28·75
H	12·40	13·10
CH_4	10·85	10·55
N	14·95	14·60

The same experiment was repeated in Experiment 1593, the density being also 0·4, and the pressure 38·30 tons per sq. inch (5838 atmospheres), the results being for the sake of comparison placed alongside those of Experiment 1586.

These results I consider quite satisfactory, but the comparison with Explosive IV. was even closer.

In Experiment 1598 a charge of Explosive IV. was fired under a density of 0·4 and a pressure of 43·2 tons per sq. inch (6585 atmospheres), the percentage volumes of the permanent gases being :—

	Experiment 1598.	Experiment 1599.
	per cent.	per cent.
CO_2	34·40	34·40
CO	27·65	27·75
H	13·10	13·15
CH_4	8·98	8·95
N	15·87	15·75

In Experiment 1599 the same explosive was fired at the same density, the pressure being 40·76 tons per sq. inch (6213 atmospheres), and the percentage volumes are placed alongside those of the previous experiment. The two analyses are practically identical.*

When explosives are fired in a gun, the chamber in which the charge is placed is, of course, full of air, and in my experiments the charges were similarly treated.

With the view, however, of testing the difference due to the presence of air, I fired three charges of cordite all at a density of 0·05 (this density of course including the largest percentage of air), the three experiments being, first, with air; second, air exhausted; third, with an atmosphere of nitrogen.

The analysis gave the following results :—

---

[*] These results have been further confirmed by several other duplicate experiments.

	Experiment 1380.	Experiment 1520.	Experiment 1521.	
	Atmosphere of air.	Vessel exhausted.	Atmosphere of nitrogen.	Constituents other than nitrogen.
	per cent.	per cent.	per cent.	per cent.
CO_2	27·15	26·35	25·90	26·45
CO	34·35	35·05	34·90	35·70
H	17·50	19·50	18·45	18·85
CH_4	0·30	0·60	0·50	0·50
	79·30	81·50	79·75	81·50
N	20·70	18·50	20·25	—
	100·00	100·00	100·00	—
H_2O	2·65 grammes	2·51 grammes	2·52 grammes	—

The percentage of nitrogen is, of course, higher in Experiment 1521 than in 1520. After correcting in the former the other constituents for this difference, it will be noted from the last column that the experiment in nitrogen yielded slightly more carbon monoxide and slightly less hydrogen than did the charge fired in the exhausted vessel. The CO_2 and CH_4 are practically identical in the two experiments.

It may be interesting to compare the foregoing results with the analysis of the gases taken from the chamber of a 9·2-inch gun fired with a charge of 103 lbs. (46·71 kilos), giving a muzzle velocity of 2,600 f/s. (792·5 m/s.), and a pressure of 16·1 tons per sq. inch (2453 atmospheres).

As soon as possible after firing the muzzle of the gun was closed and the breech opened. An exhausted gas tube held in a special holder was introduced to the far end of the chamber, and one of its stop-cocks momentarily opened.

The analysis gave the following composition of the gases after deducting air : —

	Round 1.	Round 2.	Round 3. *	Round 4.
CO_2	25·7	25·4	26·0	26·5
CO	35·4	36·25	38·5	34·75
H	19·4	18·65	20·0	16·95
CH_4	0·7	0·3	0·5	0·3
N	18·8	19·4	15·0	21·5

* Results probably not very accurate owing to great dilution with air.

The samples for the first two rounds were taken so soon as the breech was opened, the last two after a dummy shot was rammed home. The composition of the gas after deducting the air is similar to that obtained by firing cordite at low densities in a closed vessel. It follows that atmospheric combustion had not taken place to any extent.

Although for the elucidation of the laws which govern the transformation of the explosives when fired I have taken the densities named, I must point out that the requirements of the artillerist are confined to much narrower limits, the density, of course, varying considerably with the particular explosive used.

In modern guns, for example, the chamber density varies from about 0·310 to nearly 0·500, a good deal of the variation being due to the nature of the explosive used. It is hardly necessary to point out to artillerists that the chamber density is not the density which is responsible for the pressure developed in the gun.

The difference, which is frequently very considerable, is due to the time taken by the explosive to burn, and this depends upon the nature, form, and dimensions of the explosive, the expansion suffered by the nascent gases and the heat lost, due to work done upon the projectile and by communication of heat to the gun, and under these circumstances the pressure developed would, with full charges if compared with close vessel pressures, represent densities approximately between 0·17 and 0·23.

The tables which are given in my late communication* to the Royal Society gave, for each particular density, the actual result observed. In the present paper the observations have been corrected by drawing curves to represent as nearly as possible the whole of the results, the actual observations, which are also given, showing in each case the departure from the curve. See Plates 10, 11, and 12.

If reference be made to the tables, or to the plates just mentioned, it will be observed how wide are the differences, not only in the absolute volumes of the several gases, but in the variations with reference to the densities at which they were fired.

Thus, for example, comparing Explosives III. and V. (Norwegian 165 and Italian ballistites, see Plate 10), while in the former the carbon monoxide commences at the density 0·05 with a percentage volume of 38·5, falling at a density of 0·45 to 22 per cent., the carbon dioxide commences with 13·3 per cent., rising rapidly to 31 per cent. In the latter explosive the CO commences at 20·5 per cent. and falls slowly to 15 per cent., while the CO_2 commences a little over 26 per cent., rising also comparatively slowly to nearly 34 per cent.

I may remark in passing that the Italian ballistite is the only explosive with which I have experimented, where, at low densities, the volume of CO_2 is greater than that of CO.

But there are in these two explosives other remarkable differences. Thus, in the Italian ballistite, at a density of 0·05, the volume of methane, CH_4, is a mere trace, about 0·02 per cent., but it remains very much lower than is the case with any other explosive, being only 1·9 per cent. at the density of 0·45. With the Norwegian, on the other hand, the CH_4, although the volume at commencement is only 0·4 per cent., is, at 0·45 density, 11 per cent.

Again, as might be expected from the large quantity of CH_4 found, in the case of the Norwegian ballistite, the volume of hydrogen falls from over 20 per cent. to about 9 per cent., in the Italian the H rises from about 8 per cent. to about 10 per cent., falling slightly at higher densities.

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* 'Phil. Trans.,' A, vol. 205, pp. 221 to 223.

In both explosives the N is practically constant at about 12 per cent. and 16 per cent. respectively, but there is a very great difference as regards the H_2O. In the Norwegian the H_2O is constant at 14 per cent., there being no greater difference than might be expected from errors of observation, while in the Italian the H_2O, which commences at density 0·05 with a volume of 29 per cent., falls at a density of 0·45 to about 24·5 per cent. No other explosive approaches the Italian ballistite in respect to the large volume of aqueous vapour formed, especially at low densities.

As regards the other explosives, the differences, although not so pronounced as those I have just quoted, are still remarkable. Thus, comparing Cordite Mark I and Norwegian 167 (see Plate 11), in the cordite the volume of CO_2 commences at 21 per cent., rising to 31½ per cent. at $d = 0·45$, while CO, commencing at 26½ per cent., falls to 16½ per cent., the two gases being of equal volume at a density of 0·19. In the case of Norwegian 167, the CO_2 commences at 15½ per cent., rising to 31 per cent., while the CO, commencing at 35½ per cent., rapidly falls to 21 per cent., the two gases being equal in volume at a density of about 0·34.

H_2O and N may, in both explosives, be regarded as nearly constant, H_2O being with the first at a volume of about 21 per cent., with the latter at a volume of about 15½ per cent., N at volumes of approximately 15·3 per cent. and 13 per cent.

CH_4 rises from a trace in I. and IV. explosives to 5·5 per cent. in the case of cordite and to 9 per cent. in the case of the Norwegian, while the H falls from nearly 16 per cent. to 10·5 per cent. in I. and from 19 per cent. to 9·5 per cent. in the case of IV.

With respect, however, to Explosives II. and VI. (M.D. and nitrocellulose) there is, in the transformation, a remarkable similarity. In both explosives (see Plate 12) the CO_2 rises from about 15 per cent. to about 29½ per cent., while the CO falls from about 35 per cent. to between 21 and 22 per cent., equal volumes being at the densities of about 0·32 and 0·36 respectively.

In both the marsh gas rises from a trace to about 9 per cent., while the hydrogen falls from about 20 per cent. to about 11 per cent. In both the H_2O and N are nearly constant, the H_2O being about 17 per cent. in each, while the N is about 12½ per cent. with M.D., and about 11½ with nitrocellulose.

In the tables are given the cubic centimetres per gramme of the permanent and total gases, and in Plate 13 are drawn curves representing for the six explosives the observations of these total volumes. It will be noted that in the case of the nitrocellulose and Norwegian ballistite 165 there is, with increasing density, a very considerable decrease in volume, but with the Italian ballistite throughout the range of the experiments there is hardly any change. The curves in this plate, it will be observed, are concave to the axis of abscissæ.

In the tables are shown the units of heat both for the water fluid and the water gaseous, and in Plate 14 are drawn curves of the units of heat, water gaseous, for the whole of the six explosives.

The Italian ballistite develops more heat than any of the other explosives, being a little higher than Mark I cordite. This is, of course, objectionable as regards erosion, but recently, when in Italy, I was informed that this heat had been greatly reduced by the incorporation of $12\frac{1}{2}$ per cent. of carbon.

I had already made some experiments with percentages of carbon, introduced as suggested by Lord Rayleigh.

The curves in this instance are all convex to the axis of abscissæ, and it is interesting to note that where the volume of gas per gramme is large the units of heat are low, and that where the volumes of gas are rapidly decreasing the curves representing the amount of heat developed show a rapid increase.

Thus, with the new explosives, the point to which I so often drew attention in the case of the great variety of the old gunpowders with which I experimented is confirmed, namely that, with an explosive, if ever a large volume of gas is formed the heat developed will be low, if a small volume be generated the heat developed will be high.

Coming now to the relation existing between the density of the charge and the pressure developed by the explosion, I have had some difficulty in regard to the abnormal pressures obtained with some explosives at high densities, but it must be remembered that the pressures to which I refer are very far above those with which artillerists are concerned, and do not materially affect the conditions of service of the propellants used in this or other countries.

If reference be made to the tables, or preferably Plate 19, it will be observed that, up to densities of 0·45, the Explosives I., II., and VI. are perfectly regular; there are no abnormal pressures in any of the three, and the curves fairly represent the observations. In the case of cordite, which has a considerably higher potential energy than the other two, I have, without any abnormal pressure, gone to densities of 0·5 and 0·55, representing pressures of 53 and 60 tons per sq. inch (8078 and 9145 atmospheres), but when M.D. and nitrocellulose were fired at the density of 0·5, the pressure of M.D. rose to 57 tons per sq. inch (8688 atmospheres) instead of the normal pressure, which should be about 49 tons per sq. inch (7469 atmospheres), and the pressure of the nitrocellulose rose to 56 tons per sq. inch (8535 atmospheres) instead of to what should have been the normal, about 47 tons per sq. inch (7164 atmospheres).

Referring again to the same plate, on which are also drawn curves representing the relation of pressure to density of Explosives III., IV., and V., it will be seen that, while the Italian ballistite follows approximately, up to a density of 0·45, the same law as rules in Explosives I., II., and VI., the two Norwegian ballistites show an abnormal, though small, increase in pressure when the density exceeds 0·3, Norwegian 167, for example, gradually approaches the cordite pressure, and at the density of 0·45 apparently equals it.

The point now to be considered is: Are these slight increments of pressure in the Norwegian ballistites, and the much more abnormal increments in Explosives II. and VI. at densities of 0·5, real, or are they due either to partial detonation or to wave action on the crusher gauge during explosion?

Supposing there to be no detonation or violent motion of the gases, the pressure on the walls of the explosive cylinder should be dependent, in a vessel impervious to heat, solely on the quantity of gas produced and on the amount of heat generated by the explosion.

I have, therefore, calculated for the whole of the explosives the value of the products (volume of gas multiplied by units of heat water gaseous) and the results are shown in Plate 15.

It will be observed that the curves, which are very nearly straight lines, practically confirm the pressure curves of Explosives I., II., V. and VI., and they equally show that the abnormal pressures of II. and VI. at densities of 0·5 are not confirmed.

To test this latter point further, I repeated the experiments with M.D. and R.R. at the density of 0·5, so arranging the lighting of the charge that the rush of the nascent gases should not impinge directly on the crusher gauge. At the same time, to be certain that the transformation was the same, the usual course of analysing the products of explosion was followed. I give the results of R.R. as an illustration. It will be seen that the pressure indicated by the gauge was in this experiment normal, and, the transformation being the same, it follows that the high pressure obtained in the first experiment was due to wave action.

Experiment 1513.		Experiment 1607.	
Density	0·5	Density	0·5
	Tons per sq. inch.		Tons per sq. inch.
Pressure	56·00	Pressure	46·48
Atmospheres	8535	Atmospheres	7084
Permanent gases.	Percentage.	Permanent gases.	Percentage.
CO_2	38·75	CO_2	38·10
CO	24·75	CO	25·00
H	10·20	H	10·70
CH_4	12·00	CH_4	11·85
N	14·30	N	14·35

The repetition of the same density, 0·5, with M.D. was not so successful, the pressure not being considerably reduced.

I may point out also that the curves appear to show that the pressures determined at the very low densities are too small, although it is true this might have been predicted. At low densities the small charge burns much more slowly, has a large percentage of air to heat up, and, from the slow burning, parts with a much greater percentage of heat to the walls of the explosion vessel.

The extraordinary rapidity with which the gases part with their heat may be appreciated if I mention that a charge of 32 grammes, giving rise to a pressure of close upon 8 tons (1219 atmospheres), parts with half of its heat to the walls of the explosion vessel in little more than half a second.

Since, with the Norwegian ballistites, there is a slight departure from previous experience, and from the pressures indicated by multiplying the volume of gas by the heat generated for densities higher than 0·3, I have shown for these explosives both the curves derived from the actual observations and that which would result if the pressure were determined from the data to which I have referred.

The next point we have to consider is: The data being as is shown in the tables and graphically in the plates, what temperature are we to assign to that generated by the explosion? With the view of studying the question I resorted to two methods: (i.) Knowing with very considerable accuracy the units of heat (water gaseous) generated by the explosion, and having determined approximately the specific heat of the gases, the temperature of explosion should be given by the equation

$$t = \frac{\text{gramme units of heat}}{\text{specific heat}} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1).$$

(ii.) Knowing also with considerable accuracy the pressure at any given density, and knowing the pressure p_0 when the volume of gas generated is reduced to the temperature of 0° C. and a pressure of 760 millims. of mercury, the temperature is given by the equation

$$t = \frac{p - p_0}{0{\cdot}00367 \times p_0} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

With reference to equation (1), the specific heat of CO_2 is a very important factor in this determination, and the recent researches of Messrs. HOLBORN and AUSTIN upon the specific heat of gases at constant pressure at high temperatures having apparently shown that the specific heats given by MALLARD and LE CHATELIER for temperatures above 100° C. are considerably too high, I have taken the figures given by these physicists, which, I may observe, up to temperatures of 800° C. are confirmed by LANGEN.

The equation given by HOLBORN and AUSTIN for the specific heat of CO_2 at constant pressure is

$$\text{Specific heat} = 0{\cdot}2028 + 0{\cdot}000{,}128{,}4\theta - 0{\cdot}000{,}000{,}05\theta^2,$$

θ being the temperature.

The correctness of this equation for temperatures up to 800° C. has been proved, and assuming that the same equation holds up to 1300° C., the specific heats for each 100 degrees are given below.

θ, temperature.	Specific heat, constant pressure.	Δ_1.	Δ_2.
° C.			
0	0·2028		
		0·0134	
100	0·2162		0·0010
		0·0124	
200	0·2286		0·0010
		0·0114	
300	0·2400		0·0010
		0·0104	
400	0·2504		0·0011
		0·0093	
500	0·2597		0·0010
		0·0083	
600	0·2680		0·0010
		0·0073	
700	0·2753		0·0010
		0·0063	
800	0·2816		0·0010
		0·0053	
900	0·2869		0·0010
		0·0043	
1000	0·2912		0·0010
		0·0033	
1100	0·2945		0·0010
		0·0023	
1200	0·2968		0·0010
		0·0013	
1300	0·2981		0·0010
		0·0003	
1400	0·2984		

It will be observed from this table that, although between 0° C. and 1400° C. there is a large increase in the value of the specific heat, yet the increments per 100 degrees are rapidly decreasing, vanishing altogether at about 1400° C., at which temperature* there would be partial dissociation at atmospheric pressure. The temperature would, however, probably require to be considerably higher at the pressures we are considering.

The specific heats given are, as I have said, those for constant pressure, and to obtain those at constant volume it is necessary to divide by the constant k connecting the specific heats of gases and vapours at constant pressure and constant volume.

I give below the values I have used (1) of the specific heats at constant pressure—these are taken either from HOLBORN and AUSTIN's paper, or from LANDOLT-

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* MENDELEEF, 'Principles of Chemistry,' vol. 1, p. 381; also DEVILLE, 'Comptes Rendus,' vol. 56, p. 729; and BERTHELOT, 'Comptes Rendus,' vol. 68, p. 1035.

Börnstein, 'Physikalisch-chemische Tabellen,' 1905; (2) of the constant *k*—these are all taken from Landolt, pp. 407–8; (3) of the specific heats at constant volume.

Gases, &c.	Specific heat, constant pressure.	Value of *k*.	Specific heat, constant volume.
CO_2	0·2986	1·282	0·232
CO	0·2425	1·401	0·173
H	3·4100	1·408	2·422
CH_4	0·5922	1·316	0·450
N	0·2497	1·410	0·177
H_2O	0·4210	1·330	0·361

The specific heats calculated from the above data of the gases generated by the explosion of the six propellants are given in the tables, embodying the results of the whole of the experiments for each propellant, and in the tables are also given the temperatures of explosion deduced from equations (1) and (2), and here again it must be remembered that the temperatures with which artillerists are chiefly concerned are those due to densities varying approximately between 0·17 and 0·23.

For the sake of clearness, the temperatures obtained from equations (1) and (2) are graphically shown on Plates 16, 17, and 18.

Beginning with equation (1)—the Italian ballistite, which shows the highest temperature, commences at the density of 0·05 with 4943° C., this temperature hardly varying at all till the density of 0·25 is reached, when it slowly but regularly increases to about 5000° C. at $d = 0·45$. Cordite Mark I, commencing at 4742° C. with a very slight fall, is practically constant up to $d = 0·30$, after which it rises somewhat rapidly to a temperature of 4921° C. at $d = 0·45$ and to 5060° C. at $d = 0·50$.

M.D., commencing with 3814° C. with a slight fall, reaches the same temperature at $d = 0·22$, after which it rises rapidly to about 4455° C. at $d = 0·45$.

Norwegian ballistite 167 begins about 3748° C., and, with a very slight fall, regains the same temperature at $d = 0·2$, after which it reaches 4298° C. at $d = 0·45$ and 4437° C. at $d = 0·50$.

Norwegian ballistite 165 has a temperature 350° C. lower between densities 0·05 and 0·15, and, after the latter density, rises rapidly to 4177° C. at $d = 0·45$ and to 4325° C. at $d = 0·5$.

The nitrocellulose R.R., commencing at 3213° C., rises steadily, but not very rapidly, to 3861° C. at $d = 0·45$ and to 3977° C. at 0·5.

When, however, we come to the temperatures given by equation (2), we are met with some very remarkable differences, which are shown by the tables, but which are more readily appreciated if reference be made to Plates 16, 17, and 18, in which the explosives are arranged in descending order of the temperatures developed.

It will be observed that at the higher densities and pressures there is generally a very tolerable accordance in the temperatures obtained from the two formulæ, but as the density and pressure diminish the divergence becomes, in all cases, considerable, but very greatly more with the explosives which develop very high temperatures and which give rise to large percentages of carbonic anhydride.

The only construction I am able to put upon the tolerably close approximation of temperature given by the two formulæ at high densities and pressures, and the wide differences which exist in some of the explosives at low densities, is that, as I think it reasonable to expect, at high densities dissociation of the carbonic anhydride is prevented by the very high pressure, and that the great difference between, for instance, Italian ballistite and nitrocellulose R.R. at, say, the density of 0·1, is due, firstly, to the difference of the temperature at which the nascent gases are generated, and, secondly, to the proportion of CO_2 which is subject to dissociation.

Formula (1) gives for Italian ballistite at $d = 0{\cdot}1$ a temperature of nearly 5000° C., and for this explosive the temperature given by units of heat/by specific heat is nearly constant, while the percentage of CO_2 is 38·2. The same formula gives for the nitrocellulose at the same density a temperature of formation of 3200° C., while the percentage of CO_2 is only 19·45.

I have pointed out that, under atmospheric pressure, the dissociation of CO_2 commences at about 1300° C., and the very much higher temperatures of formation of the gases of the Italian ballistite, combined with its double percentage of CO_2, appear to me to be sufficient to explain the results obtained with this explosive.

If reference be made to Plate 16, it will be seen that while at the density of 0·1 there is, with Italian ballistite, a difference of about 1800° C. between the two formulæ, there is with the nitrocellulose a difference only of under 800° C.

The theory I venture to submit is as follows :—

The nascent gases are generated at temperatures approximately as given by equation (1) and by the red curves in Plates 16, 17, and 18.

Under the low densities and pressures at the very high temperatures with which we are concerned, the CO_2 and possibly some H_2O are partially dissociated, giving rise to the fall in temperature exhibited by the results obtained from equation (2) at low densities. At high densities, as already pointed out, the two equations give, in some cases, accordant results, in all cases tolerable agreement; it therefore appears to me to be reasonable to suppose that the facts I have recorded are due to partial dissociation at low densities and pressures, which dissociation is prevented by the very high pressures ruling at densities of 0·40, 0·45, and 0·50.

As no free oxygen is ever found in the analysis, in cooling down any free oxygen due to dissociation must have combined and the heat lost by dissociation regained. The re-combination must, however, be very gradual, as no discontinuity is observed in the cooling curves.

A certain amount of confirmation is given to the view I have taken by the fact that if the explosives be arranged according to the amount of heat generated, derived from equation (1), regard being also had to the amount of CO_2 found, it will be found that the differences between the two formulæ decrease approximately as the factors to which I have referred decrease, as is shown in the following table:—

(1) Explosives.	(2) Temperature of formation derived from equation (1). Density = 0·05.	(3) Percentage of CO_2.	(4) Temperature reduced by dissociation derived from equation (2). Density = 0·05.	(5) Difference of temperature.
	° C.		° C.	° C.
Italian ballistite . . .	4943	37·05	2745	2198
Cordite Mark I . . .	4742	27·20	2800	1942
M.D.	3814	18·40	2345	1469
Norwegian 167 . . .	3748	18·45	2200	1548
Norwegian 165 . . .	3410	15·60	2000	1410
Nitrocellulose	3213	17·95	2260	953

The differences given in column (5) of the above table represent, for the very low density of 0·05, the differences which I suppose to be due chiefly to dissociation, but partly to the communication of heat to the explosion vessel—but these differences are very considerably less if the mean density giving rise to the maximum pressure in the bores of guns is taken. Thus with Italian ballistite the difference between the two formulæ is approximately 1210° C.; with cordite Mark I, 860° C.; with M.D., 560° C.; with Norwegian 167, 600° C.; with Norwegian 165, 510° C.; and with nitrocellulose R.R., 480°.

At the density of 0·45 the differences between the two formulæ are as follows:—

		° C.
Italian ballistite	difference	150,
Cordite Mark I	,,	200,
M.D.	,,	320,
Norwegian ballistite 167	,,	250,
Norwegian ballistite 165	,,	130,
Nitrocellulose	,,	180.

It will be observed, both from the above figures and the curves, that with the Italian ballistite alone at the density 0·45 is the temperature derived from equation (2) lower than that derived from equation (1). With all the other explosives the temperatures derived from equation (2) are the higher. The differences, however, are not great, being generally under 5 per cent., that is about 200° C.

In the case of experiments carried on, both at pressures and temperatures very greatly above the limits at which physicists ordinarily experiment, I can hardly hope that the methods I have employed, and the conclusions at which I have arrived, will escape criticism.

The results of the experiments given in the tables and plates may, however, be taken as very approximately correct, and the repeat experiments I have made show that there is great constancy in the transformation which takes place on explosion at any given density.

I conclude by expressing my obligation to Dr. SODEAU and Mr. HUTCHINSON for their assistance in carrying out the various experiments, in the analysis, and in the laborious, but necessary calculations.

NOTE.—In the case of the Norwegian ballistites, the pressures at densities above 0·3 have been corrected to accord with the values obtained from the volume of the gas generated, multiplied by the units of heat determined.

APPENDIX.

Abstract of Experiments Referred to in Paper.

ITALIAN BALLISTITE.

Experiment 1528.—Fired in explosion vessel R, 15 grammes of Italian ballistite. Density of charge 0·05.
Pressure 3·22 tons per sq. inch (490·8 atmospheres).
Permanent gases 9186·4 cub. centims. at 0° C. and 760 millims.
Aqueous vapour 3843·9 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	3·256	9·515	0·442	2·604
Originally in ballistite . . .	3·444	9·588	0·422	2·359
Differences	−0·188	−0·073	+0·020	+0·245

Experiment 1527.—Fired in explosion vessel R, 30 grammes of Italian ballistite. Density of charge 0·10.
Pressure 6·42 tons per sq. inch (978·5 atmospheres).
Permanent gases 18,565·1 cub. centims. at 0° C. and 760 millims.
Aqueous vapour 6599·4 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	6·585	18·506	0·806	4·984
Originally in ballistite . . .	6·717	18·698	0·823	4·602
Differences	−0·132	− 0·192	−0·017	+0·382

Experiment 1523.—Fired in explosion vessel R, 45 grammes of Italian ballistite. Density of charge 0·15. Pressure 11·67 tons per sq. inch (1778·7 atmospheres).

Permanent gases 27,251·0 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 9421·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	9·607	27·126	1·182	7·265
Originally in ballistite . . .	9·840	27·393	1·206	6·741
Differences	−0·233	− 0·267	−0·024	+0·524

Experiment 1525.—Fired in explosion vessel R, 60 grammes of Italian ballistite. Density of charge 0·20. Pressure 15·45 tons per sq. inch (2354·9 atmospheres).

Permanent gases 36,559·0 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 12,654·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	12·847	36·643	1·609	9·607
Originally in ballistite . . .	13·220	36·802	1·621	9·057
Differences	− 0·373	− 0·159	−0·012	+0·550

Experiment 1526.—Fired in explosion vessel R, 75 grammes of Italian ballistite. Density of charge 0·25. Pressure 20·65 tons per sq. inch (3147·4 atmospheres).

Permanent gases 46,276·5 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 15,102·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	16·270	45·666	1·971	12·016
Originally in ballistite . . .	16·535	46·030	2·027	11·327
Differences	− 0·265	− 0·364	−0·056	+ 0·689

Experiment 1530.—Fired in explosion vessel R, 90 grammes of Italian ballistite. Density of charge 0·30.

Pressure 26·35 tons per sq. inch (4016·3 atmospheres).

Permanent gases 55,293·0 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 17,801·6 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	19·490	54·558	2·361	14·427
Originally in ballistite . . .	19·789	55·088	2·426	13·551
Differences	− 0·299	− 0·530	−0·065	+ 0·876

Experiment 1531.—Fired in explosion vessel R, 120 grammes of Italian ballistite. Density of charge 0·40.

Pressure 40·29 tons per sq. inch (6141·0 atmospheres).

Permanent gases 73,046·5 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 22,902·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	25·990	72·788	3·152	18·922
Originally in ballistite . . .	26·320	73·280	3·230	18·030
Differences	− 0·330	− 0·492	−0·078	+ 0·892

Experiment 1605.—Fired in explosion vessel Q, 126·9 grammes of Italian ballistite. Density of charge 0·45.

Pressure 45·57 tons per sq. inch (6945·8 atmospheres).

Permanent gases 76,776·7 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 24,569·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	27·637	77·436	3·436	20·035
Originally in ballistite . . .	28·000	77·946	3·433	19·181
Differences	− 0·363	− 0·510	+0·003	+ 0·854

NORWEGIAN 165.

Experiment 1577.—Fired in explosion vessel R, 15 grammes of Norwegian ballistite. Density of charge 0·05.

Pressure 2·49 tons per sq. inch (379·5 atmospheres).

Permanent gases 12,778·1 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 2139·7 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	4·212	8·533	0·476	2·404
Originally in ballistite . . .	4·375	8·664	0·500	2·086
Differences	−0·163	−0·131	−0·024	+0·318

Experiment 1576.—Fired in explosion vessel Q, 31 grammes of Norwegian ballistite. Density of charge 0·10.

Pressure 6·30 tons per sq inch (960·2 atmospheres).

Permanent gases 26,017·1 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 4242·0 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	8·611	17·502	0·991	4·601
Originally in ballistite . . .	8·878	17·582	1·015	4·233
Differences	−0·267	− 0·080	−0·024	+0·368

Experiment 1534.—Fired in explosion vessel Q, 46·5 grammes of Norwegian ballistite. Density of charge 0·15.

Pressure 10·19 tons per sq. inch (1553·2 atmospheres).

Permanent gases 37,894·3 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 6120·5 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	12·969	26·211	1·503	6·583
Originally in ballistite . . .	13·233	26·206	1·512	6·309
Differences	− 0·264	+ 0·005	−0·009	+0·274

Experiment 1536.—Fired in explosion vessel Q, 62 grammes of Norwegian ballistite. Density of charge 0·20.

Pressure 14·62 tons per sq. inch (2228·4 atmospheres).

Permanent gases 49,158·5 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 8036·2 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	17·143	34·967	2·056	8·787
Originally in ballistite . . .	17·600	34·856	2·012	8·392
Differences	– 0·457	+ 0·111	+0·044	+0·395

Experiment 1539.—Fired in explosion vessel Q, 77·5 grammes of Norwegian ballistite. Density of charge 0·25.

Pressure 18·77 tons per sq. inch (2860·9 atmospheres).

Permanent gases 60,392·5 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 9685·8 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	21·622	44·029	2·478	10·865
Originally in ballistite . . .	22·117	43·800	2·528	10·545
Differences	– 0·495	+ 0·229	– 0·050	+ 0·320

Experiment 1540.—Fired in explosion vessel Q, 93 grammes of Norwegian ballistite. Density of charge 0·30.

Pressure 23·60 tons per sq. inch (3597·1 atmospheres).

Permanent gases 70,096·7 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 11,623·9 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	25·889	53·121	2·988	12·706
Originally in ballistite . . .	26·517	52·513	3·031	12·643
Differences	– 0·628	+ 0·608	– 0·043	+ 0·063

Experiment 1593.—Fired in explosion vessel Q, 124 grammes of Norwegian ballistite. Density of charge 0·40.

Pressure 38·30 tons per sq. inch (5837·6 atmospheres).

Permanent gases 88,638·0 cub centims. at 0° C. and 760 millims.

Aqueous vapour 14,733·9 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	34·452	70·736	4·032	16·233
Originally in ballistite . . .	35·130	69·570	4·015	16·750
Differences	− 0·678	+ 1·166	+0·017	− 0·517

Experiment 1600.—Fired in explosion vessel R, 135 grammes of Norwegian ballistite. Density of charge 0·45.

Pressure 46·96 tons per sq. inch (7157·5 atmospheres).

Permanent gases 93,232·7 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 15,226·5 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	37·292	76·242	4·367	17·777
Originally in ballistite . . .	37·996	75·246	4·342	18·116
Differences	− 0·704	+ 0·996	+0·025	− 0·339

NORWEGIAN 167.

Experiment 1581.—Fired in explosion vessel Q, 15·5 grammes of Norwegian 167. Density of charge 0·05.

Pressure 2·61 tons per sq. inch (397·8 atmospheres).

Permanent gases 12,539·9 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 2,639·8 cub. centims.

RECONCILIATION.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	4·172	9·080	0·490	2·541
Originally in ballistite . . .	4·347	9·182	0·505	2·247
Differences	−0·175	−0·102	−0·015	+0·294

Experiment 1580.—Fired in explosion vessel R, 30 grammes of Norwegian 167. Density of charge 0·10.

Pressure 6·71 tons per sq. inch (1022·7 atmospheres).

Permanent gases 24,036·6 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 4274·4 cub. centims.

Reconciliation.

	C.	O.	H.	N
	grammes	grammes	grammes	grammes
Found by analysis	8·047	17·167	0·900	4·584
Originally in ballistite . . .	8·196	17·313	0·952	4·236
Differences	−0·149	− 0·146	−0·052	+0·348

Experiment 1570.—Fired in explosion vessel Q, 46·5 grammes of Norwegian 167. Density of charge 0·15.

Pressure 10·04 tons per sq. inch (1530·3 atmospheres).

Permanent gases 37,070·7 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 6924·1 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	12·531	26·956	1·440	7·092
Originally in ballistite . . .	12·821	27·083	1·489	6·627
Differences	− 0·290	− 0·127	−0·049	+0·465

Experiment 1535.—Fired in explosion vessel Q, 62 grammes of Norwegian 167. Density of charge 0·20.

Pressure 14·83 tons per sq. inch (2260·4 atmospheres).

Permanent gases 48,402·3 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 8770·2 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	16·671	35·897	1·941	9·138
Originally in ballistite . . .	17·000	35·910	1·974	8·786
Differences	−0·329	− 0·013	−0·033	+0·352

Experiment 1538.—Fired in explosion vessel Q, 77·5 grammes of Norwegian 167. Density of charge 0·25.

Pressure 19·43 tons per sq. inch (2961·5 atmospheres).

Permanent gases 58,686·9 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 10,890·0 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	20·587	44·534	2·403	11·074
Originally in ballistite . . .	21·050	44·466	2·444	10·880
Differences	− 0·463	+ 0·068	−0·041	+ 0·194

Experiment 1537.—Fired in explosion vessel R, 90 grammes of Norwegian 167. Density of charge 0·30.

Pressure 25·62 tons per sq. inch (3905·0 atmospheres).

Permanent gases 66,328·5 cub. centims at 0° C. and 760 millims.

Aqueous vapour 12,634·0 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	24·045	52·133	2·816	12·730
Originally in ballistite . . .	24·499	51·750	2·844	12·662
Differences	− 0·454	+ 0·383	−0·028	+ 0·068

Experiment 1599.—Fired in explosion vessel R, 120 grammes of Norwegian 167. Density of charge 0·40.

Pressure 40·66 tons per sq. inch (6197·4 atmospheres).

Permanent gases 82,640·9 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 15,793·8 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	31·590	68·493	3·710	16·328
Originally in ballistite . . .	32·072	67·748	3·724	16·577
Differences	− 0·482	+ 0·745	−0·014	− 0·249

Experiment 1601.—Fired in explosion vessel R, 135 grammes of Norwegian 167. Density of charge 0·45.

Pressure 47·46 tons per sq. inch (7233·9 atmospheres).

Permanent gases 92,430·5 cub. centims. at 0° C. and 760 millims.

Aqueous vapour 17,785·5 cub. centims.

Reconciliation.

	C.	O.	H.	N.
	grammes	grammes	grammes	grammes
Found by analysis	35·911	77·970	4·284	18·899
Originally in ballistite . . .	36·600	77·312	4·249	18·917
Differences	− 0·689	+ 0·658	+0·035	− 0·018

ITALIAN BALLISTITE.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme		583·0	600·0	604·5	605·5	606·0	604·5	603·0	602·0	600·0	597·0
Volumes of total gases per gramme		824·2	816·0	811·7	810·5	808·1	804·5	800·0	793·9	788·3	780·0
Percentage volumes of permanent gases	CO_2	37·05	38·20	39·15	39·95	40·50	41·10	42·15	43·40	44·70	46·20
	CO	28·85	27·40	26·15	25·00	24·10	23·35	22·20	20·95	19·30	17·55
	H	11·55	12·65	13·25	13·60	13·90	13·75	13·60	13·00	12·40	11·70
	CH_4	0·12	0·15	0·35	0·50	0·60	1·00	1·35	2·00	2·85	3·75
	N	22·43	21·60	21·10	20·95	20·90	20·80	20·70	20·65	20·75	20·80
Percentage volumes of total gases	CO_2	26·20	27·90	29·05	30·20	31·00	31·68	32·45	33·15	33·85	34·50
	CO	20·54	20·04	19·48	18·73	18·10	17·40	16·65	15·70	14·80	13·90
	H	8·18	9·23	9·78	10·10	10·31	10·30	10·05	9·90	9·60	9·20
	CH_4	0·10	0·18	0·24	0·32	0·49	0·72	1·00	1·50	2·00	2·60
	N	15·93	15·85	15·70	15·50	15·50	15·50	15·55	15·65	15·75	15·90
	H_2O	29·05	26·80	25·75	25·15	24·60	24·40	24·30	24·10	24·00	23·90
Percentage weights of total gases	CO_2	42·50	44·73	46·30	47·50	48·63	49·60	50·80	51·80	52·68	53·50
	CO	21·20	20·72	19·95	19·20	18·40	17·60	16·55	15·60	14·65	13·65
	H	0·60	0·66	0·70	0·74	0·75	0·75	0·73	0·70	0·66	0·62
	CH_4	0·06	0·09	0·15	0·19	0·28	0·40	0·60	0·90	1·16	1·53
	N	16·50	16·14	16·00	15·92	15·88	15·85	15·80	15·70	15·65	15·55
	H_2O	19·14	17·66	16·90	16·45	16·06	15·80	15·52	15·30	15·20	15·15
Pressure in tons per sq. inch		3·00	6·50	10·85	15·45	20·65	26·30	32·60	39·10	45·57	52·20
Pressure in atmospheres		457·3	990·7	1653·7	2354·9	3147·5	4008·7	4968·9	5959·6	6945·8	7956·3
Units of heat, water fluid		1330·3	1308·5	1302·5	1305·0	1309·0	1312·0	1319·5	1327·4	1335·3	1345·5
Units of heat, water gaseous		1227·7	1213·9	1211·9	1216·8	1222·9	1227·3	1236·3	1245·4	1253·8	1264·3
Specific heat		0·2484	0·2483	0·2489	0·2497	0·2502	0·2506	0·2510	0·2512	0·2515	0·2518
Temperatures of explosion (I.)		4943°	4889°	4869°	4873°	4888°	4897°	4926°	4955°	4980°	5025°
Temperatures of explosion (II.)		2745°	3060°	3380°	3686°	3972°	4235°	4466°	4655°	4805°	4930°

CORDITE MARK I.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme		670·0	692·5	699·0	697·0	688·0	671·5	658·0	644·9	634·0	623·6
Volumes of total gases per gramme		870·0	878·5	880·0	875·5	865·0	848·0	832·5	820·0	809·5	798·8
Percentage volumes of permanent gases	CO_2	27·20	28·10	29·00	30·85	32·60	34·70	36·60	38·50	40·20	41·90
	CO	34·35	33·25	31·80	29·95	27·90	25·85	24·15	22·55	20·90	19·40
	H	17·52	19·05	19·65	19·40	18·85	17·65	16·35	14·90	13·50	12·00
	CH_4	0·23	0·45	0·80	1·35	2·10	3·00	3·95	4·95	6·00	7·00
	N	20·70	19·15	18·75	18·45	18·55	18·80	18·95	19·10	19·40	19·70
Percentage volumes of total gases	CO_2	21·07	21·98	23·13	24·37	25·87	27·64	29·30	30·56	31·60	32·48
	CO	26·46	26·13	25·20	23·91	22·31	20·44	18·75	17·46	16·35	15·43
	H	13·53	15·12	15·60	15·53	14·96	13·93	12·70	11·73	10·60	9·47
	CH_4	0·23	0·32	0·54	1·00	1·65	2·45	3·21	3·98	4·75	5·54
	N	15·97	15·08	14·93	14·86	14·90	14·95	15·04	15·11	15·35	15·60
	H_2O	22·74	21·37	20·60	20·33	20·31	20·59	21·00	21·16	21·35	21·48
Percentage weights of total gases	CO_2	36·10	38·15	40·20	42·15	44·25	46·10	47·65	49·10	50·35	51·65
	CO	29·00	28·55	27·50	25·82	23·79	21·80	19·82	18·05	16·45	15·20
	H	1·14	1·16	1·21	1·25	1·16	1·04	0·90	0·85	0·75	0·67
	CH_4	0·18	0·21	0·38	0·68	0·90	1·50	2·10	2·34	2·90	3·18
	N	17·63	16·93	16·40	16·10	15·95	15·76	15·68	15·66	15·60	15·50
	H_2O	15·95	15·00	14·31	14·00	13·95	13·80	13·85	14·00	13·95	13·80
Pressure in tons per sq. inch		3·25	7·00	11·70	17·00	22·75	28·90	35·05	41·35	47·30	53·30
Pressure in atmospheres		495·4	1066·9	1783·3	2591·1	3467·6	4404·9	5342·3	6302·6	7209·5	8124·0
Units of heat, water fluid		1272·3	1253·5	1244·5	1246·0	1252·5	1265·0	1282·0	1304·5	1329·0	1355·0
Units of heat, water gaseous		1186·8	1174·0	1170·0	1170·5	1177·0	1186·5	1201·0	1223·4	1252·0	1287·0
Specific heat		0·2503	0·2521	0·2531	0·2540	0·2542	0·2544	0·2546	0·2546	0·2544	0·2541
Temperatures of explosion (I.)		4742°	4665°	4620°	4608°	4625°	4665°	4720°	4800°	4920°	5060°
Temperatures of explosion (II.)		2800°	3100°	3415°	3760°	4110°	4435°	4723°	4960°	5120°	5270°

M.D. CORDITE.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme		781·8	790·0	786·5	773·0	754·0	733·5	714·0	693·5	673·5	653·5
Volumes of total gases per gramme		955·4	948·0	931·0	913·5	893·5	873·0	852·0	832·0	810·6	789·5
Percentage volumes of permanent gases	CO_2	18·40	19·90	21·65	23·95	26·55	29·05	31·45	33·90	36·30	38·45
	CO	42·50	40·75	38·65	36·35	33·80	31·25	29·15	27·00	25·00	23·15
	H	23·10	23·25	22·70	21·50	19·90	18·10	16·20	14·15	12·00	9·90
	CH_4	0·35	1·00	2·00	3·25	4·75	6·40	7·75	9·30	10·75	12·15
	N	15·65	15·10	15·00	14·95	15·00	15·20	15·45	15·65	15·95	16·35
Percentage volumes of total gases	CO_2	14·85	16·45	18·35	20·30	22·25	24·15	26·20	28·15	30·15	32·35
	CO	34·87	33·95	32·40	30·50	28·45	26·45	24·40	22·60	20·85	19·00
	H	18·95	19·20	19·00	18·00	16·65	15·00	13·45	11·80	10·15	8·45
	CH_4	0·29	0·83	1·60	2·70	3·95	5·40	6·60	7·80	8·94	9·95
	N	12·89	12·57	12·45	12·50	12·65	12·85	13·00	13·05	13·21	13·45
	H_2O	18·15	17·00	16·20	16·00	16·05	16·15	16·35	16·60	16·70	16·80
Percentage weights of total gases	CO_2	27·80	30·55	33·30	36·20	38·90	41·50	43·82	46·10	48·26	50·30
	CO	41·33	39·90	37·60	34·70	31·70	28·84	26·20	23·63	21·15	18·94
	H	1·62	1·70	1·65	1·50	1·30	1·16	1·02	0·88	0·77	0·66
	CH_4	0·18	0·55	1·05	1·80	2·60	3·35	4·04	4·64	5·22	5·70
	N	15·32	14·80	14·60	14·35	14·20	14·00	13·85	13·75	13·65	13·55
	H_2O	13·75	12·50	11·80	11·45	11·30	11·15	11·07	11·00	10·95	10·85
Pressure in tons per sq. inch		3·00	6·50	10·50	15·45	20·95	26·70	32·45	38·25	43·95	49·50
Pressure in atmospheres		457·3	990·7	1600·4	2354·9	3193·2	4069·6	4946·0	5830·1	6698·9	7544·8
Units of heat, water fluid		1035·9	1024·5	1023·5	1030·0	1044·5	1070·0	1105·0	1145·0	1194·0	1242·0
Units of heat, water gaseous		965·0	959·0	959·0	964·5	981·0	1008·0	1045·0	1090·0	1132·5	1178·0
Specific heat		0·2530	0·2544	0·2550	0·2550	0·2546	0·2544	0·2542	0·2541	0·2542	0·2544
Temperatures of explosion (I.)		3814°	3770°	3761°	3790°	3853°	3962°	4111°	4290°	4455°	4630°
Temperatures of explosion (II.)		2345°	2565°	2850°	3240°	3623°	3961°	4275°	4551°	4817°	5051°

NORWEGIAN BALLISTITE, LOT 167.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme		770·3	783·0	772·0	757·5	742·0	725·5	709·0	690·0	671·0	652·5
Volumes of total gases per gramme		932·4	924·0	914·0	899·0	880·5	861·0	841·0	820·0	803·5	782·0
Percentage volumes of permanent gases	CO_2	18·45	20·15	22·05	24·05	26·30	28·70	31·25	34·05	37·00	39·75
	CO	43·10	41·50	39·50	37·45	35·20	32·85	30·30	27·65	24·80	22·10
	H	22·00	22·30	21·85	20·90	19·40	17·55	15·50	13·45	11·40	9·40
	CH_4	0·30	0·65	1·50	2·60	4·00	5·55	7·30	8·95	10·60	12·20
	N	16·15	15·40	15·10	15·00	15·10	15·35	15·65	15·90	16·20	16·55
Percentage volumes of total gases	CO_2	15·40	16·70	18·35	20·15	22·11	24·35	26·53	28·76	30·97	33·50
	CO	35·57	34·95	33·50	31·60	29·66	27·65	25·47	23·20	20·88	18·60
	H	18·17	19·00	18·60	17·70	16·40	14·60	12·95	11·24	9·50	7·60
	CH_4	0·25	0·65	1·30	2·30	3·35	4·65	5·95	7·50	8·90	10·25
	N	13·28	12·90	12·85	12·73	12·80	12·90	13·05	13·25	13·65	13·95
	H_2O	17·33	15·80	15·40	15·52	15·68	15·85	16·05	16·05	16·10	16·10
Percentage weights of total gases	CO_2	28·51	30·85	33·10	35·60	38·29	41·05	43·75	46·50	49·05	51·65
	CO	41·60	40·35	38·40	35·80	33·20	30·15	27·10	24·00	21·05	17·75
	H	1·52	1·58	1·50	1·43	1·30	1·15	1·05	0·95	0·75	0·65
	CH_4	0·17	0·42	0·90	1·55	2·11	2·90	3·60	4·35	5·10	5·85
	N	15·70	14·95	14·70	14·42	14·05	13·75	13·65	13·60	13·75	13·95
	H_2O	12·50	11·85	11·40	11·20	11·05	11·00	10·85	10·60	10·30	10·15
Pressure in tons per sq. inch		2·70	6·50	10·40	14·70	19·75	25·50	32·25	40·00	48·10	56·75
Pressure in atmospheres		411·5	990·7	1585·1	2240·5	3010·3	3886·7	4915·5	6096·7	7331·3	8649·8
Units of heat, water fluid		1001·0	992·0	994·0	1005·5	1025·3	1050·5	1080·0	1114·5	1146·5	1180·5
Units of heat, water gaseous		934·0	928·5	932·9	945·5	966·1	991·6	1021·9	1057·7	1091·3	1126·1
Specific heat		0·2492	0·2502	0·2510	0·2518	0·2524	0·2529	0·2533	0·2536	0·2539	0·2538
Temperatures of explosion (I.)		3748°	3711°	3717°	3755°	3825°	3921°	4034°	4165°	4298°	4437°
Temperatures of explosion (II.)		2200°	2560°	2875°	3170°	3465°	3760°	4045°	4310°	4540°	4752°

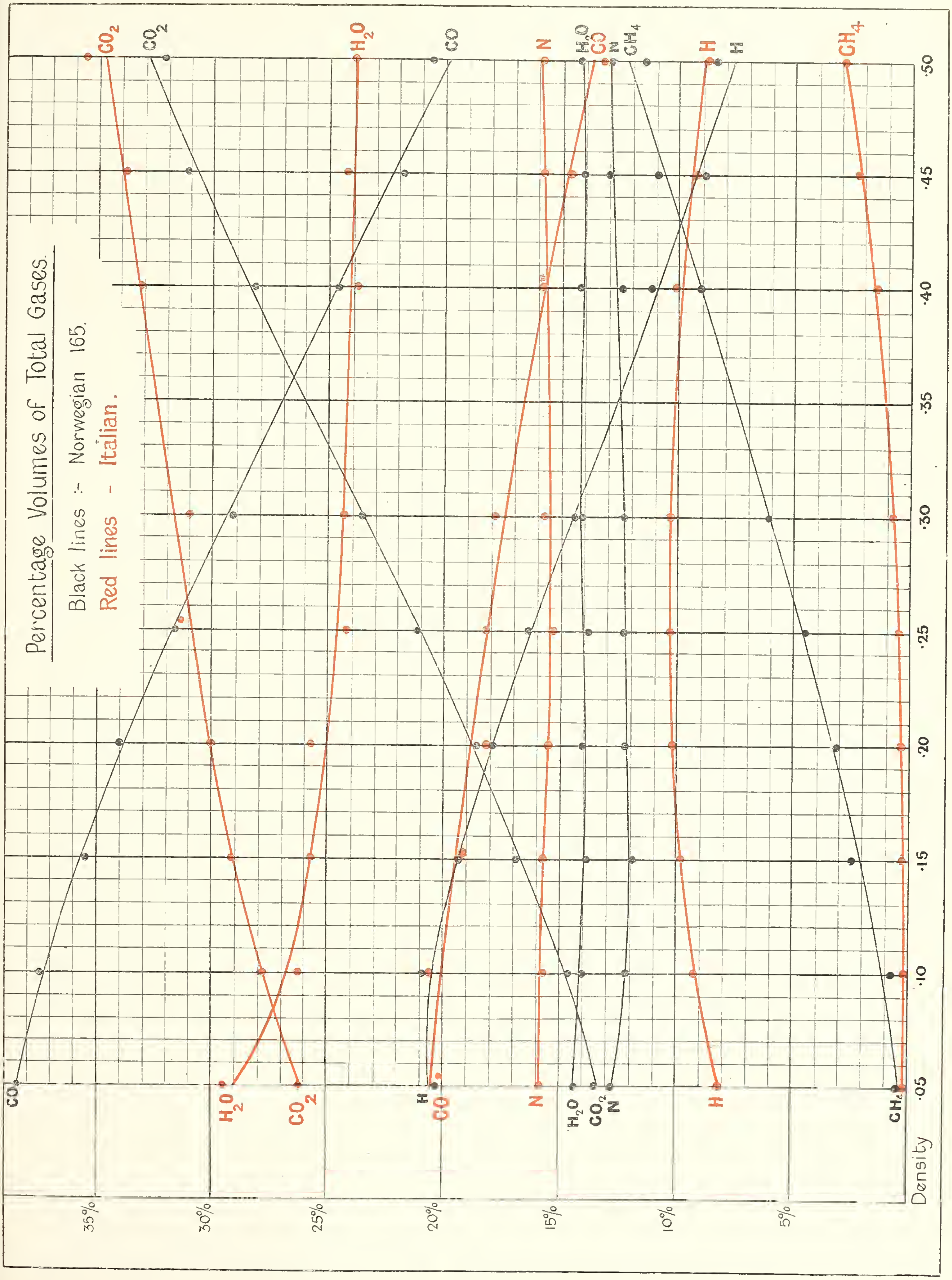
Norwegian Ballistite, Lot 165.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme . .		820·0	818·0	802·0	782·0	762·0	743·0	726·0	706·5	687·0	672·0
Volumes of total gases per gramme		959·0	950·0	931·3	909·9	887·0	864·0	844·5	821·0	801·0	780·0
Percentage volumes of permanent gases	CO_2	15·60	17·10	19·45	21·90	24·50	27·45	30·30	33·20	36·10	38·30
	CO	44·95	43·45	41·55	39·40	36·80	34·00	31·30	28·50	25·65	23·15
	H	23·75	24·15	22·75	20·95	19·00	16·95	14·85	12·70	10·65	9·00
	CH_4	0·65	1·20	2·25	3·70	5·40	7·05	8·90	10·80	12·60	14·30
	N	15·05	14·10	14·00	14·05	14·30	14·55	14·65	14·80	15·00	15·25
Percentage volumes of total gases	CO_2	13·40	14·80	16·75	18·70	21·07	23·55	26·10	28·50	30·95	33·40
	CO	38·50	37·22	35·60	33·87	31·64	29·40	26·80	24·55	21·95	19·50
	H	20·60	20·45	19·40	18·00	16·30	14·50	12·75	11·00	9·25	7·40
	CH_4	0·40	1·10	2·17	3·30	4·65	6·15	7·60	9·20	10·90	12·55
	N	12·70	12·18	12·05	12·15	12·34	12·37	12·50	12·65	12·90	13·00
	H_2O	14·40	14·25	14·03	13·98	14·00	14·03	14·25	14·10	14·05	14·15
Percentage weights of total gases	CO_2	25·25	27·75	30·77	33·80	37·10	40·25	43·50	46·24	48·95	51·40
	CO	46·12	44·25	41·75	38·65	35·15	31·78	28·35	25·15	22·00	18·85
	H	1·73	1·85	1·61	1·33	1·25	1·10	1·00	0·85	0·60	0·50
	CH_4	0·45	0·85	1·46	2·15	2·90	3·72	4·50	5·42	6·28	7·25
	N	15·42	14·45	14·00	13·89	13·70	13·40	13·10	12·97	13·00	13·00
	H_2O	11·03	10·85	10·41	10·18	9·90	9·75	9·55	9·37	9·17	9·00
Pressure in tons per sq. inch		2·55	6·15	10·10	14·40	19·00	24·00	30·45	38·30	46·96	56·00
Pressure in atmospheres .		388·7	937·4	1539·4	2194·8	2895·9	3658·0	4641·2	5837·6	7157·5	8535·5
Units of heat, water fluid		918·9	911·5	919·5	935·5	964·0	998·5	1030·0	1065·0	1101·2	1140·0
Units of heat, water gaseous		859·8	853·4	863·7	881·0	911·0	945·7	978·8	1014·8	1052·1	1091·8
Specific heat		0·2520	0·2510	0·2504	0·2503	0·2502	0·2505	0·2510	0·2514	0·2519	0·2521
Temperatures of explosion (I.)		3412°	3400°	3449°	3530°	3635°	3770°	3905°	4040°	4177°	4325°
Temperatures of explosion (II.)		2000°	2365°	2715°	3010°	3305°	3573°	3850°	4103°	4325°	4530°

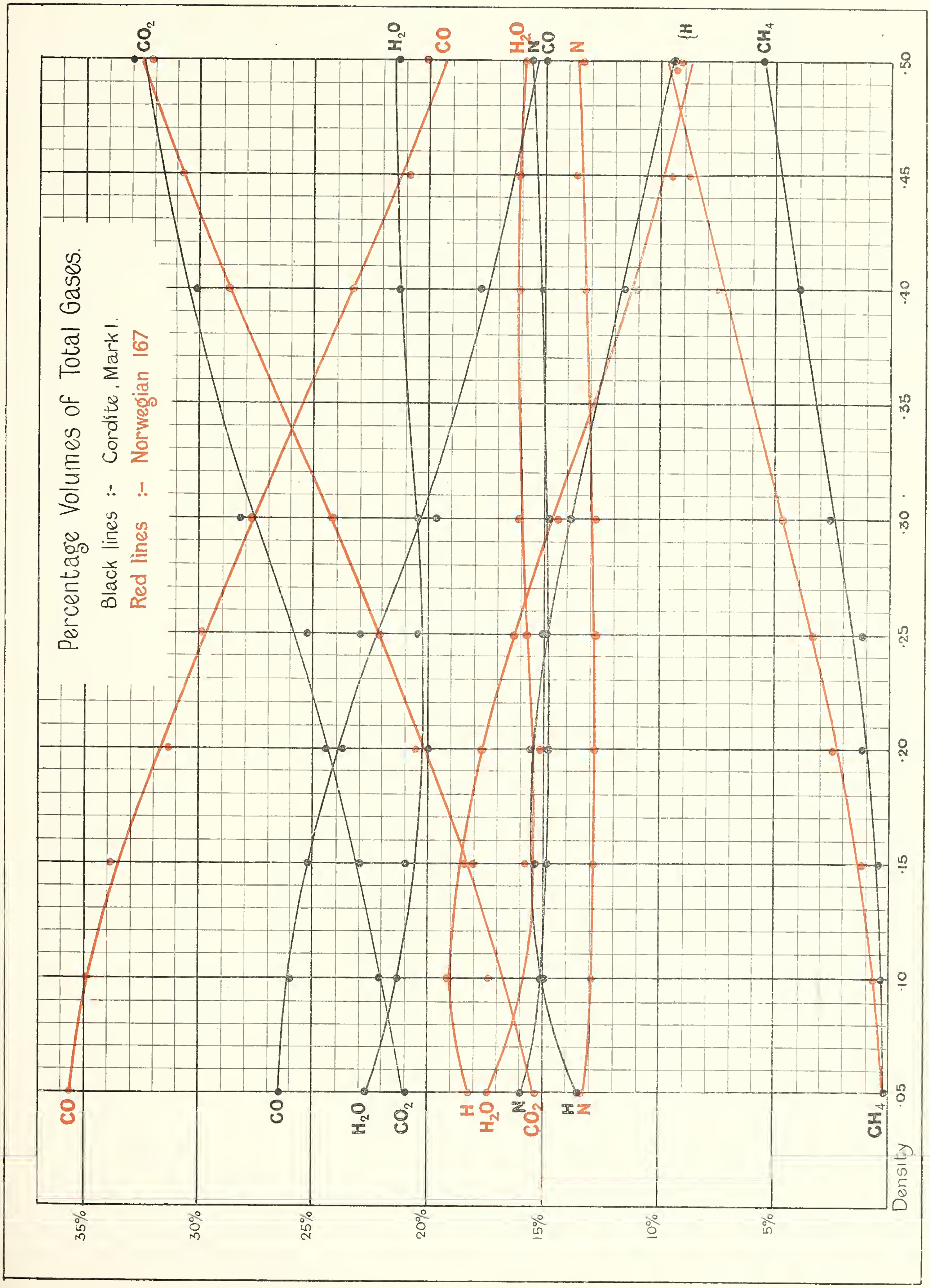
NITROCELLULOSE.

Density of charge exploded		0·05	0·10	0·15	0·20	0·25	0·30	0·35	0·40	0·45	0·50
Volumes of permanent gases per gramme . .		814·7	810·5	795·0	776·0	751·5	730·0	712·5	695·0	676·0	659·5
Volumes of total gases per gramme		993·1	980·0	958·5	934·0	906·5	883·0	862·0	841·0	821·0	802·0
Percentage volumes of permanent gases	CO_2	17·95	19·45	21·55	23·55	25·70	27·95	30·40	33·00	35·55	38·20
	CO	43·45	41·80	40·05	38·20	36·10	34·00	31·80	29·45	27·40	25·05
	H	24·45	24·80	23·70	21·65	19·15	17·10	15·36	14·10	12·75	11·80
	CH_4	0·50	1·00	1·90	3·55	5·75	7·50	9·00	10·02	10·90	11·60
	N	13·65	12·95	12·80	13·05	13·30	13·45	13·44	13·43	13·40	13·35
Percentage volumes of total gases	CO_2	14·95	16·19	17·50	19·40	21·50	23·50	25·50	27·60	29·60	31·60
	CO	35·36	34·60	33·35	31·90	29·95	28·25	26·50	24·65	22·85	20·96
	H	20·01	20·67	19·90	18·00	15·80	14·05	12·65	11·60	10·65	10·00
	CH_4	0·49	0·71	1·58	2·89	4·80	6·20	7·50	8·44	9·23	9·80
	N	11·19	10·75	10·62	10·83	11·04	11·16	11·08	11·00	11·00	11·00
	H_2O	18·00	17·08	17·05	16·98	16·91	16·84	16·77	16·71	16·67	16·64
Percentage weights of total gases	CO_2	28·25	30·45	32·70	35·15	37·40	39·95	42·55	45·27	47·70	50·20
	CO	43·51	41·70	39·37	36·58	33·60	30·83	28·30	25·60	23·14	20·60
	H	1·74	1·78	1·68	1·52	1·31	1·12	0·97	0·88	0·79	0·72
	CH_4	0·30	0·58	1·07	1·92	3·13	3·92	4·48	4·95	5·37	5·74
	N	13·71	12·92	12·58	12·48	12·41	12·29	12·10	11·80	11·60	11·44
	H_2O	12·49	12·57	12·60	12·35	12·15	11·89	11·60	11·50	11·40	11·30
Pressure in tons per sq. inch		3·00	6·40	9·95	13·80	18·30	22·95	28·40	34·30	40·45	46·80
Pressure in atmospheres .		457·3	975·5	1516·6	2103·4	2789·3	3498·0	4328·7	5228·0	6165·4	7133·3
Units of heat, water fluid		874·0	884·5	900·5	924·0	945·5	968·5	993·0	1018·0	1041·0	1065·0
Units of heat, water gaseous		817·5	818·0	830·0	850·5	875·5	900·5	927·5	954·5	985·0	1015·0
Specific heat		0·2544	0·2560	0·2570	0·2568	0·2564	0·2558	0·2554	0·2551	0·2551	0·2552
Temperatures of explosion (I.)		3213°	3195°	3230°	3312°	3415°	3520°	3632°	3742°	3861°	3977°
Temperatures of explosion (II.)		2260°	2415°	2590°	2815°	3060°	3335°	3590°	3832°	4033°	4212°

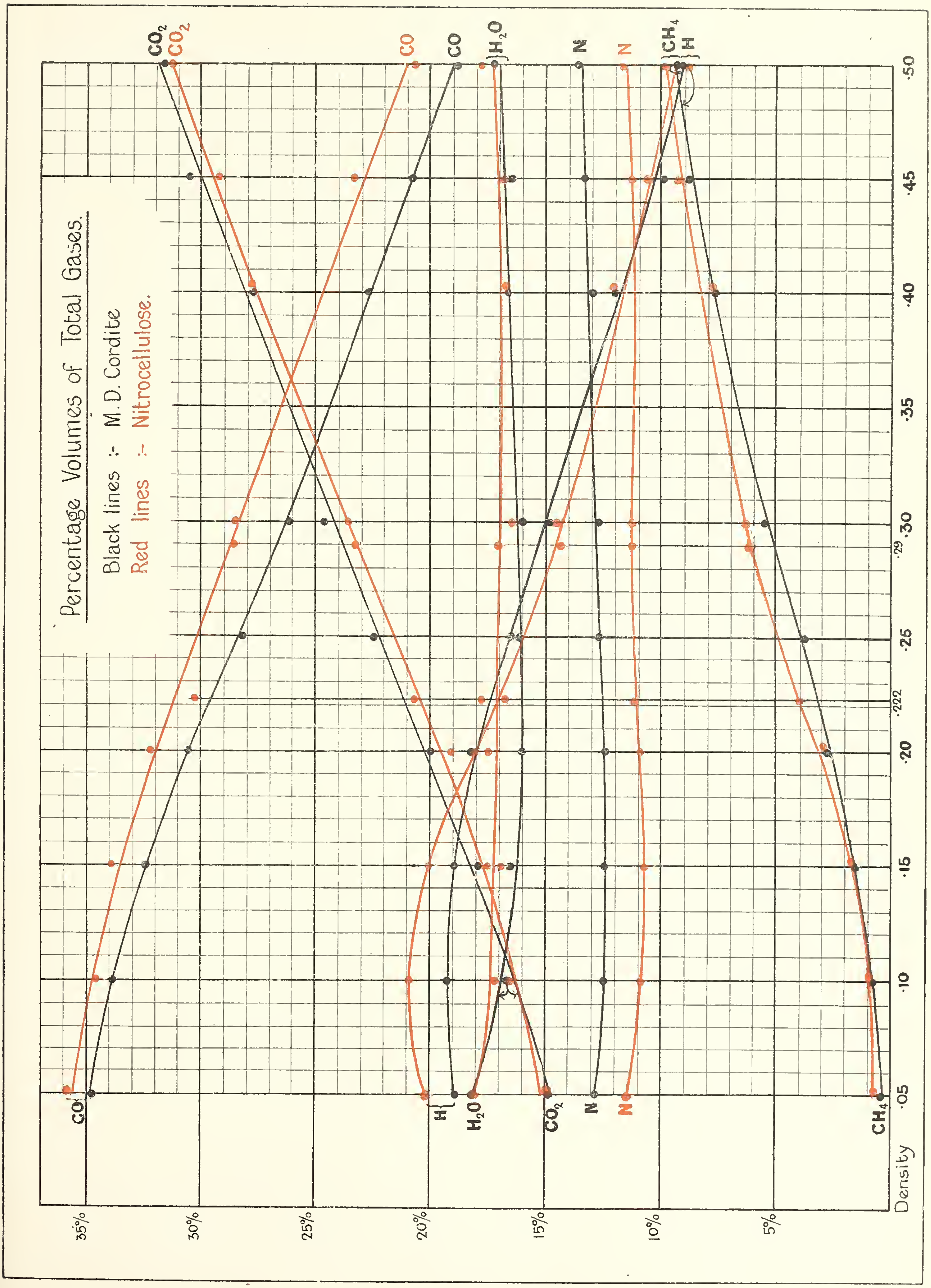
PRESENTED
7 NOV.

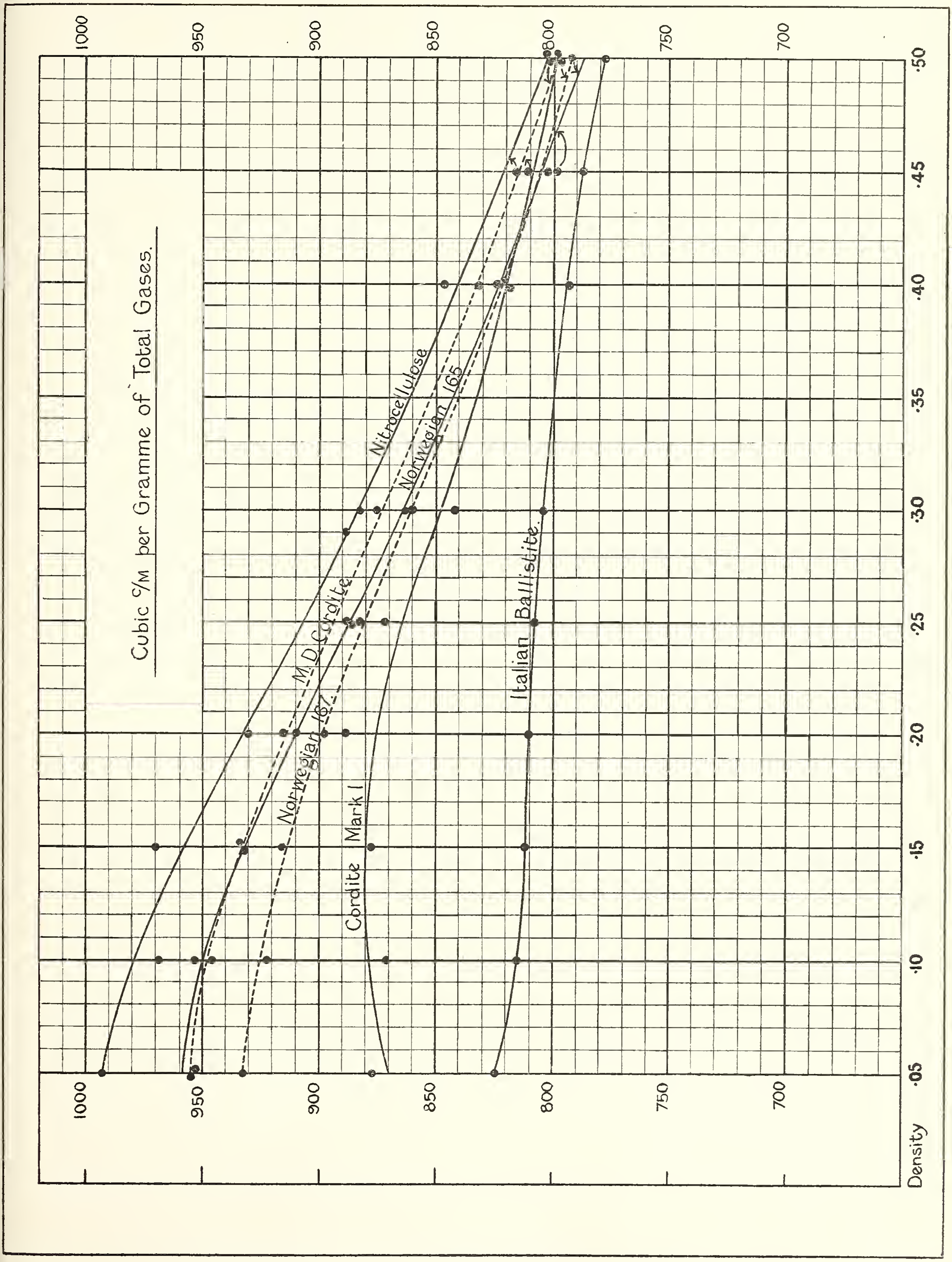

Percentage Volumes of Total Gases.
Black lines :- Norwegian 165.
Red lines - Italian.
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
35%
30%
25%
20%
15%
10%
5%
CO
H_2O
CO_2
H
CO
N
H_2O
CO_2
N
H
CH_4
CO_2
CO_2
H_2O
CO
N
H_2O
CO
N
CH_4
H
H
CH_4

NATURAL HISTORY

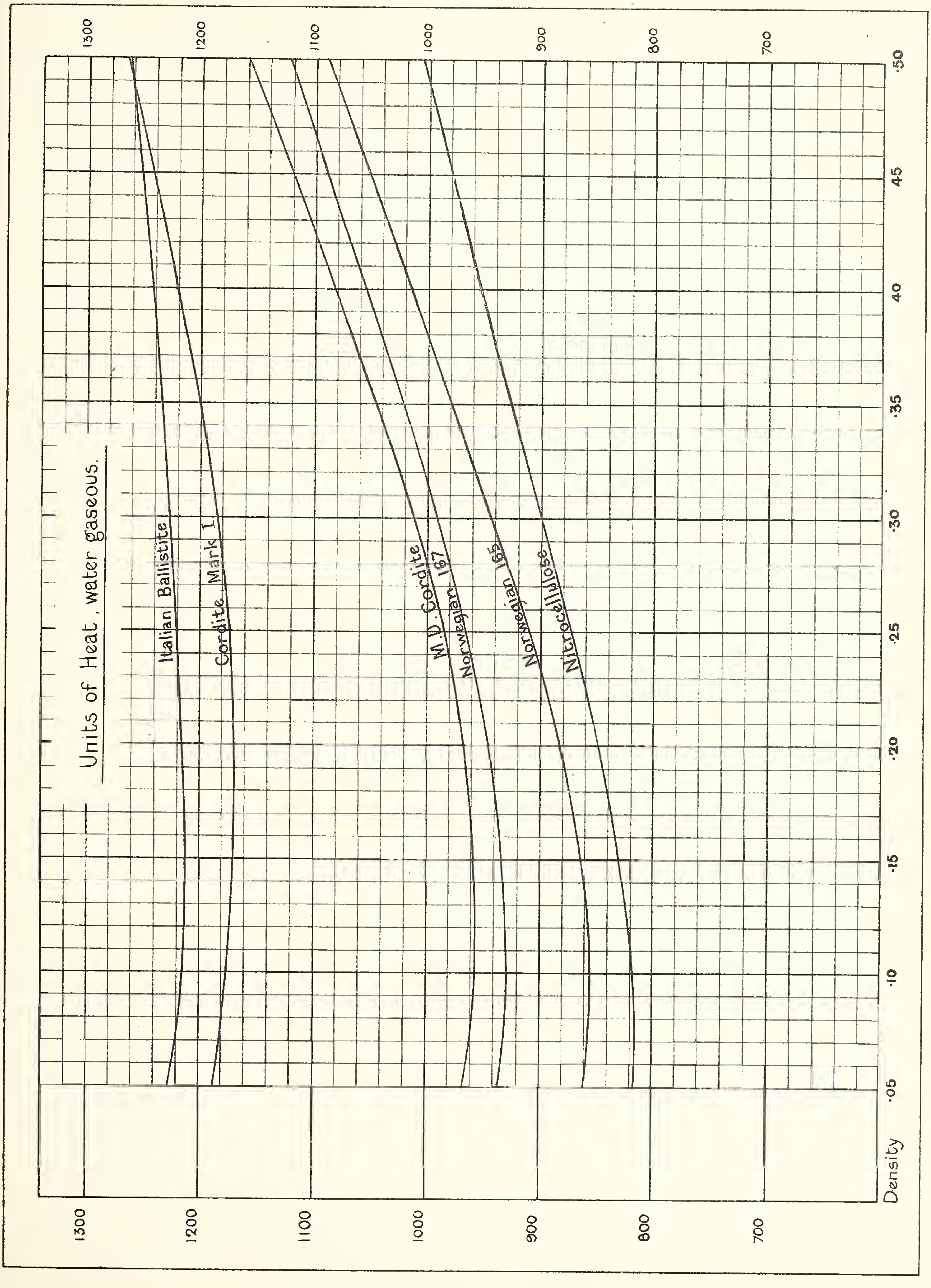

Percentage Volumes of Total Gases.
Black lines :- Cordite, Mark I.
Red lines :- Norwegian 167
35%
30%
25%
20%
15%
10%
5%
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
CO
CO
H_2O
CO_2
H
H_2O
N
CO_2
H
N
CH_4
CO_2
H_2O
CO
H_2O
N
CO
N
{H
CH_4

TURAL HISTORY

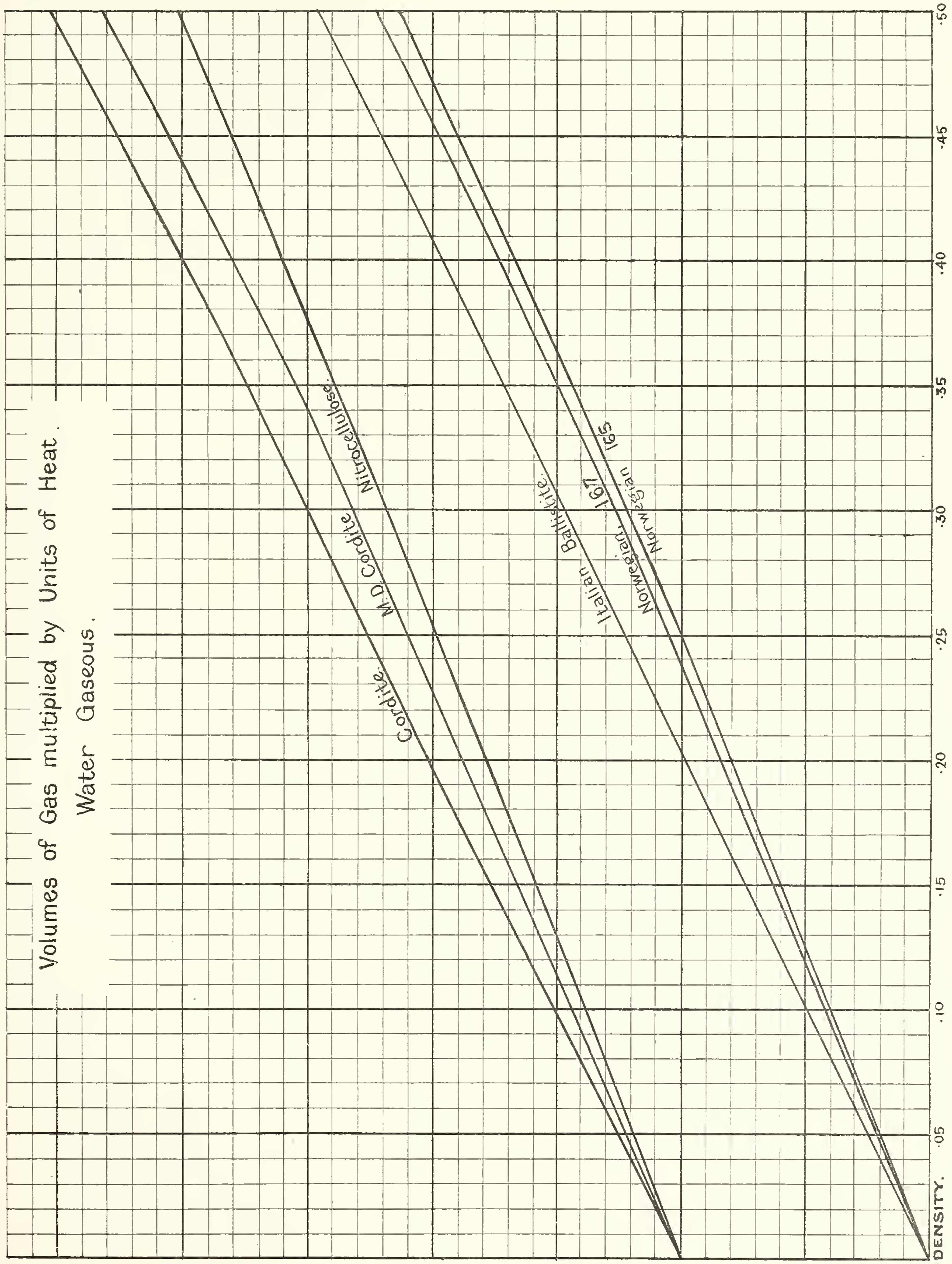

Percentage Volumes of Total Gases.
Black lines :- M.D. Cordite
Red lines :- Nitrocellulose.
CO₂
CO₂
CO
CO
H₂O
N
N
CH₄
H
CO
H
H₂O
CO₂
N
N
CH₄
Density
·05
·10
·15
·20
·222
·25
·29
·30
·35
·40
·45
·50
35%
30%
25%
20%
15%
10%
5%


Cubic C/M per Gramme of Total Gases.
Nitrocellulose
Norwegian 165
Norwegian
M.D. Cordite
Norwegian 167
Cordite Mark I
Italian Ballistite.
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
1000
950
900
850
800
750
700

MUSEUM
NATURAL HISTORY

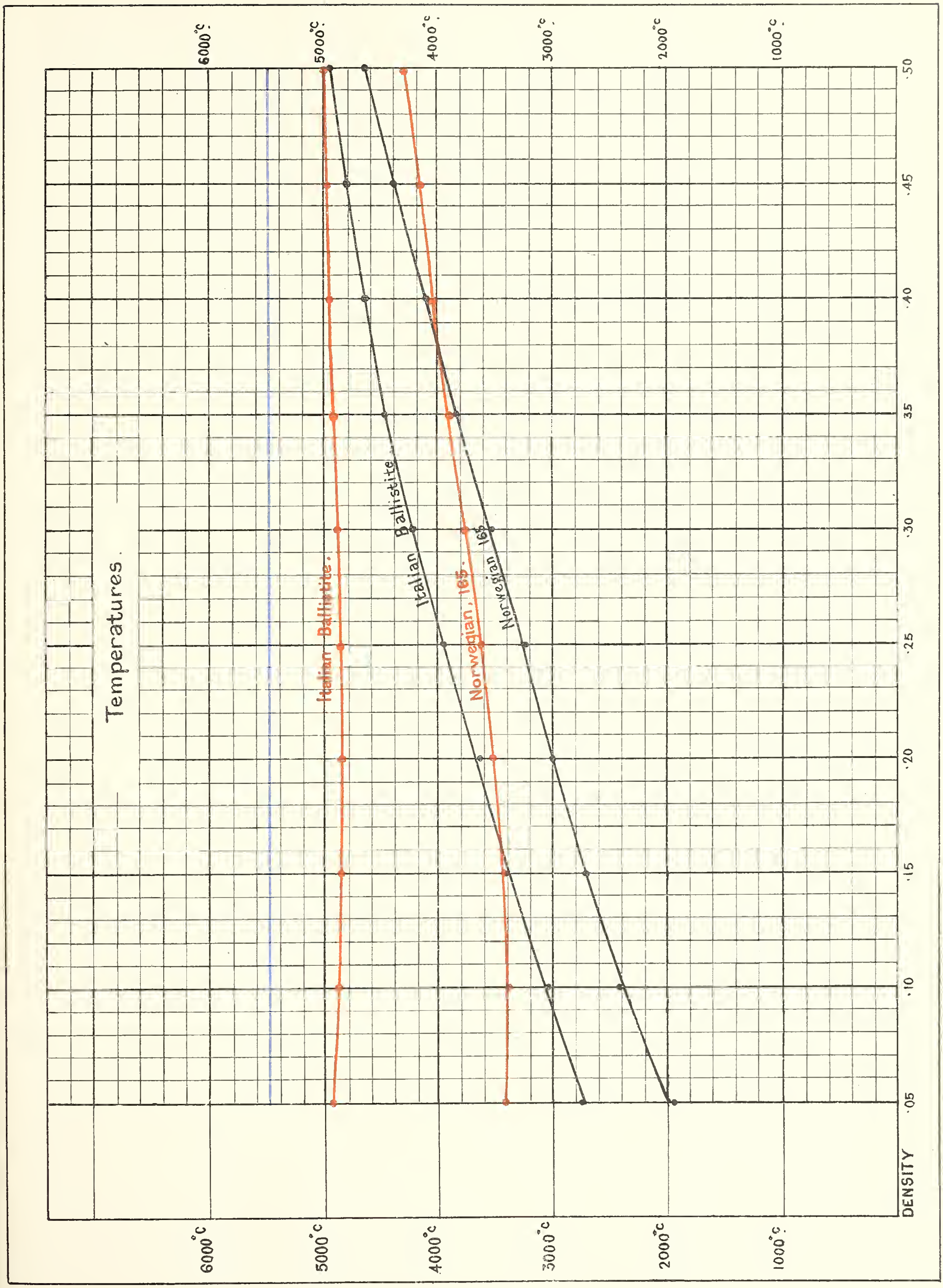

Units of Heat, water gaseous.
Italian Ballistite
Cordite, Mark I
M.D. Cordite
Norwegian 167
Norwegian 165
Nitrocellulose
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
1300
1200
1100
1000
900
800
700

MUSEUM
NATURAL HISTORY

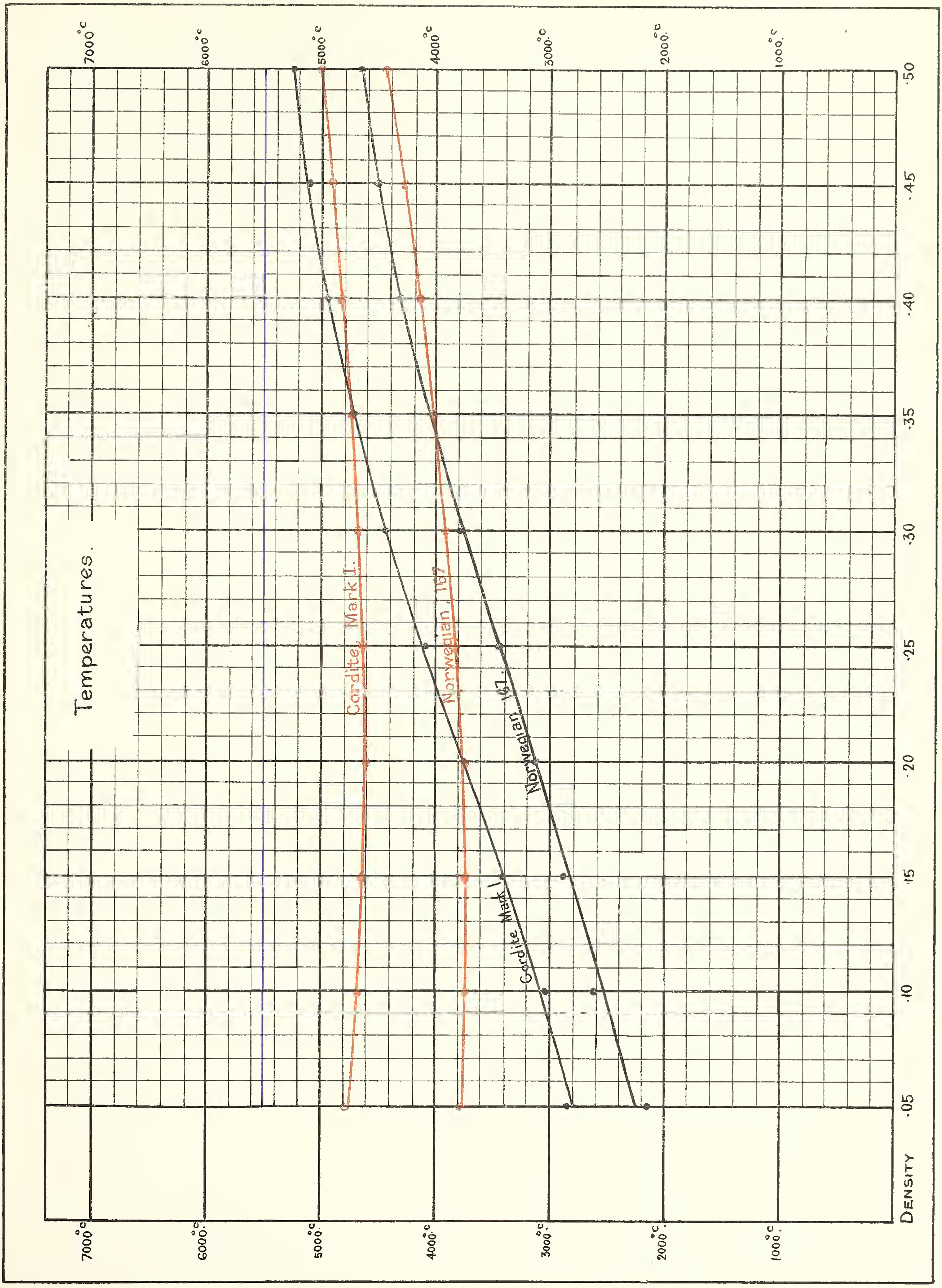


Volumes of Gas multiplied by Units of Heat.
Water Gaseous.

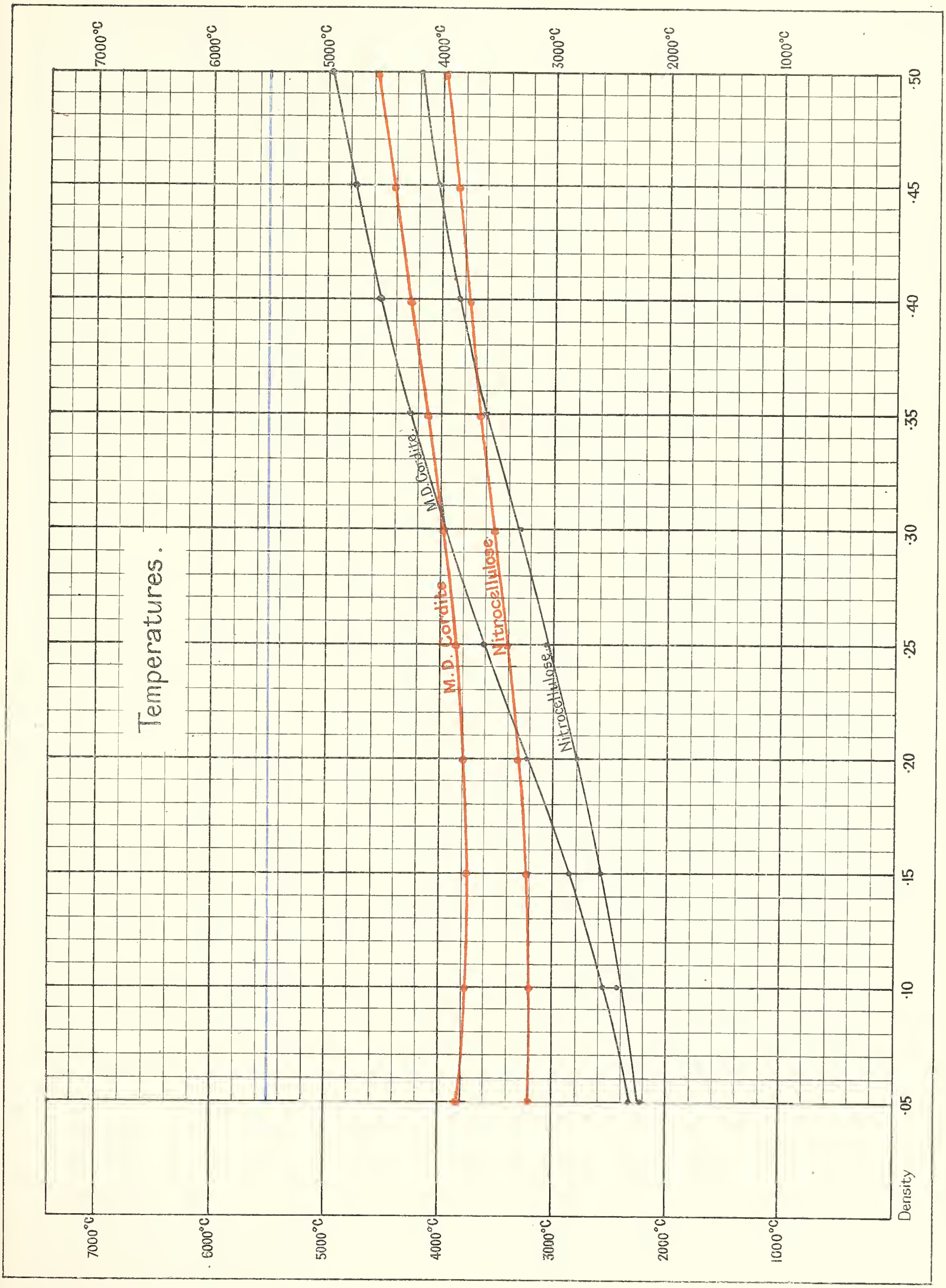
NATURAL HISTORY


Temperatures.
6000°C
5000°C
4000°C
3000°C
2000°C
1000°C
DENSITY
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
Italian Ballistite.
Italian Ballistite
Norwegian, 165.
Norwegian 165

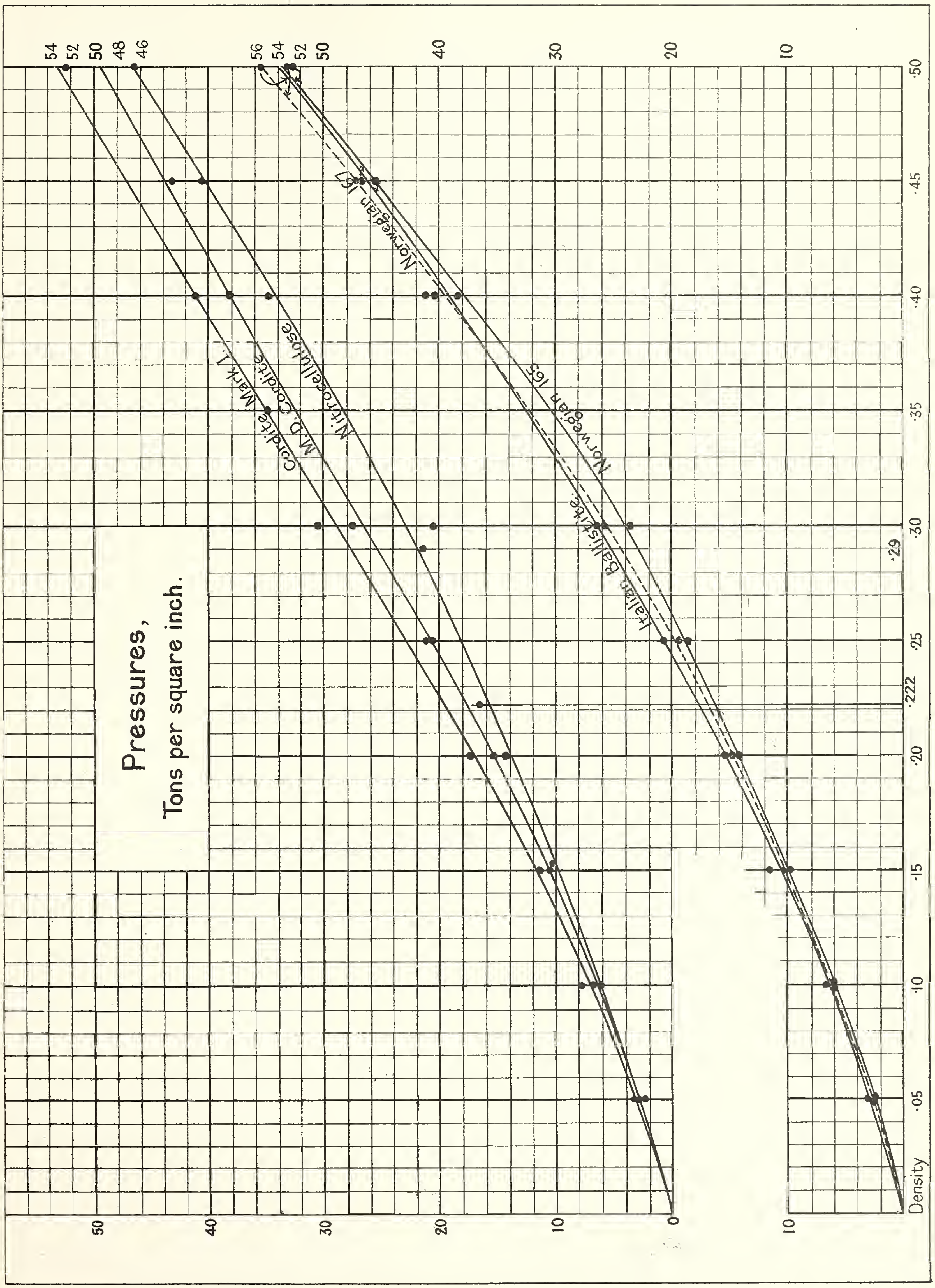
NATURAL HISTORY


Temperatures.
Cordite, Mark I.
Norwegian, 167
Norwegian 167.
Cordite Mark I
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50
1000°C
2000°C
3000°C
4000°C
5000°C
6000°C
7000°C

NATURAL HISTORY


Temperatures.
M.D. Cordite.
Nitrocellulose.
M. D. Cordite
Nitrocellulose
7000°C
6000°C
5000°C
4000°C
3000°C
2000°C
1000°C
Density
·05
·10
·15
·20
·25
·30
·35
·40
·45
·50

MUSEUM NATURAL HISTORY


Pressures,
Tons per square inch.
Density
·05
·10
·15
·20
·222
·25
·29
·30
·35
·40
·45
·50
0
10
20
30
40
50
10
20
30
40
50
52
54
56
46
48
50
52
54
Cordite Mark I
M.D. Cordite
Nitrocellulose
Norwegian 165
Norwegian 157
Italian Ballistite

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BY

THE EARL OF BERKELEY,

AND

E. G. J. HARTLEY, B.A. (OXON.).

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X. *On the Osmotic Pressures of some Concentrated Aqueous Solutions.*

By the Earl of Berkeley *and* E. G. J. Hartley, *B.A.* (*Oxon*).

Communicated by W. C. D. Whetham, *M.A.*, *F.R.S.*

Received May 28,—Read June 7, 1906.

Introduction.

In a communication* to the Royal Society by one of us it was stated that an attempt would be made to determine directly the osmotic pressures of strong solutions. The purpose for which these determinations were required was to obtain data for the tentative application of Van der Waals' equation of state to solutions, but we propose, in this communication, to restrict ourselves to the actual results obtained, reserving for a future occasion the theory of the subject.

Some time ago, in the proceedings of the Royal Society,† we gave an account of some preliminary experiments. We there described the method and apparatus we used, and at the same time stated that we hoped to get more accurate results by modifying the apparatus. This hope has been fulfilled, and we trust that a somewhat full description of the methods used both in the actual determinations and in the preparation of the membranes will, therefore, not be out of place.

Before proceeding to describe these matters, it will be advisable to discuss briefly what is meant by osmotic pressure in the case of concentrated solutions, for it appears from recent discussions‡ that there is some ambiguity about the meaning of the expression.

There seem to be two methods of investigating directly the osmotic phenomena of a solution, and these will, in general, give two different results :—

(1) One, which we may call the osmotic "force" method, depends on the determination of the rate at which the solvent will flow through a semi-permeable membrane into a large quantity of solution when there is no pressure on the latter. A knowledge of this rate together with the frictional resistance to the flow will enable the osmotic "force" to be calculated in absolute units.

---

* 'Phil. Trans. Roy. Soc.,' vol. 203, pp. 189–215.

† 'Roy. Soc. Proc.,' vol. 73, pp. 436–443.

‡ *Cf.* a letter in 'Nature,' vol. 74, p. 6.

(2) All other direct methods relate to what may be called equilibrium pressures; they depend on the measurement of the pressure to be applied to the solution to bring about a state of equilibrium between it and the solvent, when the two are separated by a semi-permeable membrane. The difference between the pressure on the solution and that on the solvent is the equilibrium pressure of the solution, under the conditions of the experiment. It is evident that, in general, for the same solution the equilibrium pressure will vary, on account of the compression of the solution and solvent, according to the pressure on the solvent. It is, therefore, necessary to state what pressure was on the solvent when the particular equilibrium pressure was observed.

We have made some attempts to obtain comparative values for the osmotic "force" by a method analogous to that indicated in (1), but these attempts, although not entirely unsuccessful, were not satisfactory, and will not be alluded to further. The following account refers only to equilibrium pressures, observed when there was a pressure of one atmosphere on the solvent.

General Description of the Method used.

A gradually increasing pressure is placed upon the solution, which is separated from the solvent by a semi-permeable membrane, until the solvent, which at first flows into the solution, reverses its direction and is squeezed out. The pressure, when there is no movement of the solvent, is considered to be the sum of the equilibrium pressure and a pressure equal to that on the solvent.

Owing to the difficulty of determining the exact point at which no movement takes place, and for other reasons, the experiments were arranged so as to enable an observation to be made of the rate of movement of the solvent both when the pressure on the solution was just below and when just above the turning-point pressure. The turning-point pressure was deduced from these two rates, or, sometimes, from a series of rates corresponding to slightly different pressures both above and below the turning-point.

The Osmotic Apparatus.

The apparatus used is shown in fig. 1. AB is a porcelain tube*, 15 centims. long, 2 centims. external and 1·2 centims. internal diameter; the vertical ends are glazed. This tube carries the semi-permeable membrane as close to the outer surface as possible. CC is a gunmetal cage against the ends of which the dermatine rings DD are compressed, when the two parts E and F of the outer gunmetal vessel are screwed together. The ends of this cage have shallow radial grooves cut out of them, so as to prevent the dermatine rings from rotating and rubbing the membrane during the operation of screwing E and F home. The length of the cage is such that, when finally set up, the dermatine rings just overlap the ends of the porcelain tube.

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* The porcelain tubes are similar in all respects to those described in our preliminary communication.

The outer gunmetal vessel (capacity about 250 cub. centims.) contains the solution which, when a pressure is applied to it, forces the dermatine rings against the bevelled faces GG, and thus causes a tight joint to be made with the porcelain tube. The joint between E and F is made good by another dermatine ring X, which is compressed between the metal ring I and the nuts JJ.

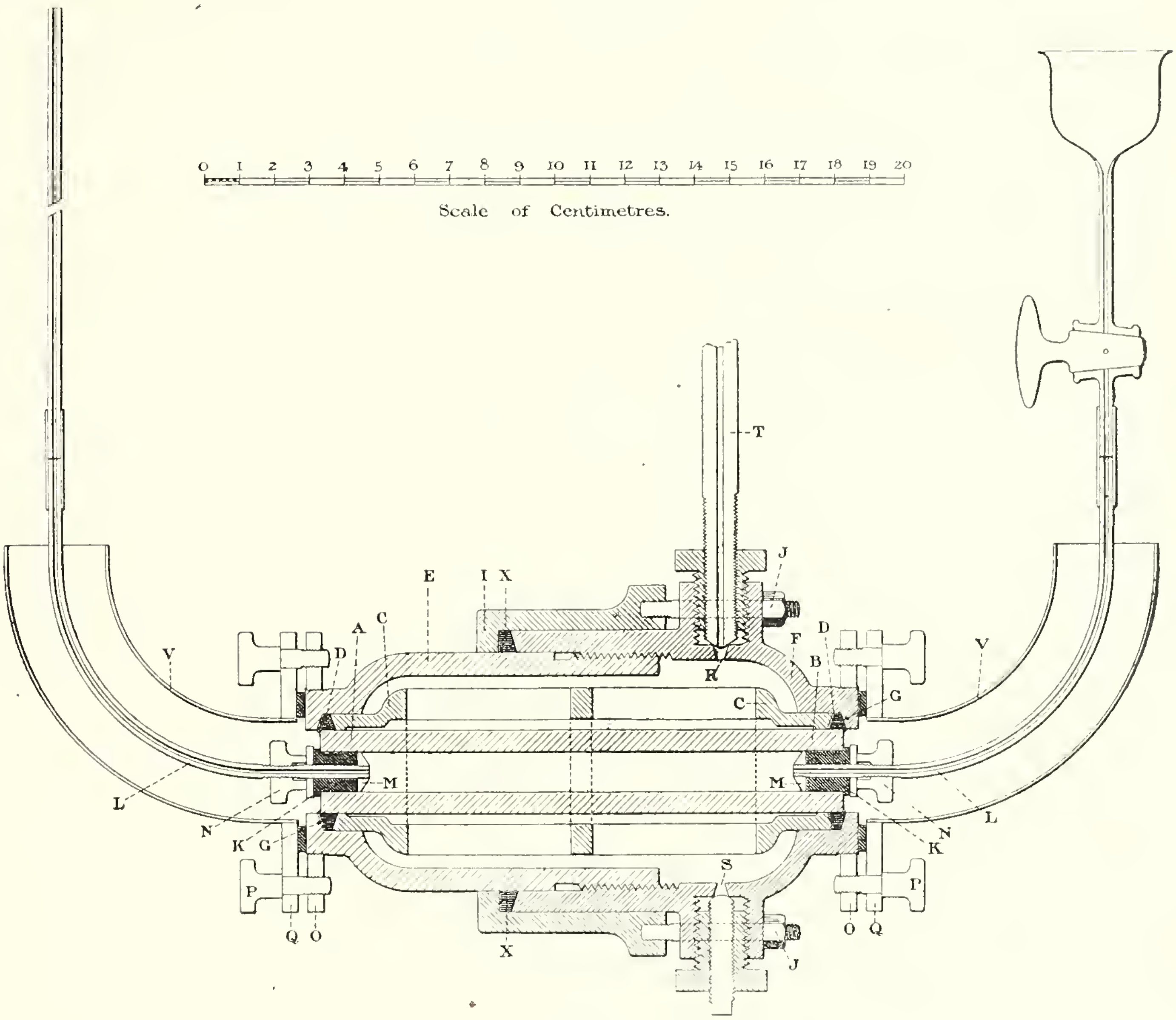

Fig. 1.

The ends of AB are closed by pieces of thick-walled rubber tubing KK, through which the brass tubes LL are passed; a water-tight joint between LL and the inside of the porcelain tube is obtained by compressing the rubber between the metal washers MM and the nuts NN.* The brass tubes are joined by rubber tubing, one to a glass tap and the other to an open glass capillary—the latter, which we shall call the water gauge, was graduated in millimetres and calibrated; one centimetre of the bore contains 0·00312 cub. centim. The outer ends of E and F have threads cut on them to receive the brass rings OO, which in their turn are perforated by screw holes to receive the thumb screws PP, by means of which, together with a rubber washer, a tight joint is made between the flanges QQ of the curved metal tubes VV and the ends of E and F. The uses of these tubes will be explained later.

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* It seems advisable to point out that the rubber tubing KK is unaffected by the pressure put upon the solution.

The perforation R is for filling the apparatus with solution, and also for connecting to the pressure apparatus, while S serves to empty the vessel. The method of making a pressure-tight joint, shown at R, originated, we believe, at the Cambridge Scientific Instrument Co. It may be useful to call attention to it, as we have experienced no trouble, although the joint has been made and remade over a thousand times. It is scarcely necessary to describe the joint, as the diagram illustrates it sufficiently; the only point to emphasize is that the thread on the steel pressure tube T should be of a smaller pitch than that on the outside of the nut.

The Beam Pressure Apparatus.

The pressure apparatus described briefly in our preliminary communication had to be modified because it was found that the dermatine-ring stuffing box therein mentioned was unsatisfactory, and also because the necessarily somewhat large leak past the stuffing box (this was unavoidable, for, if checked, the plunger was no longer free) made it imperative to adjust the beam continuously—a labour which sometimes lasted without intermission from 10 A.M. to 7 P.M.

The new form was made for us by the Cambridge Scientific Instrument Co., and is shown in elevation and plan in Diagrams 1 and 2 respectively.

Diagram 2.

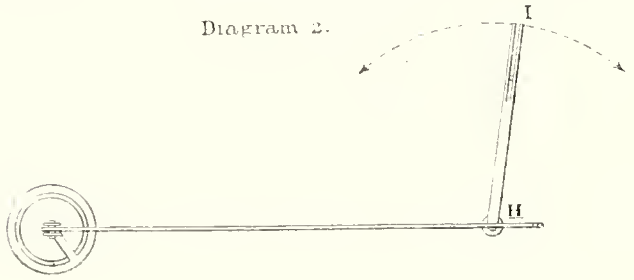
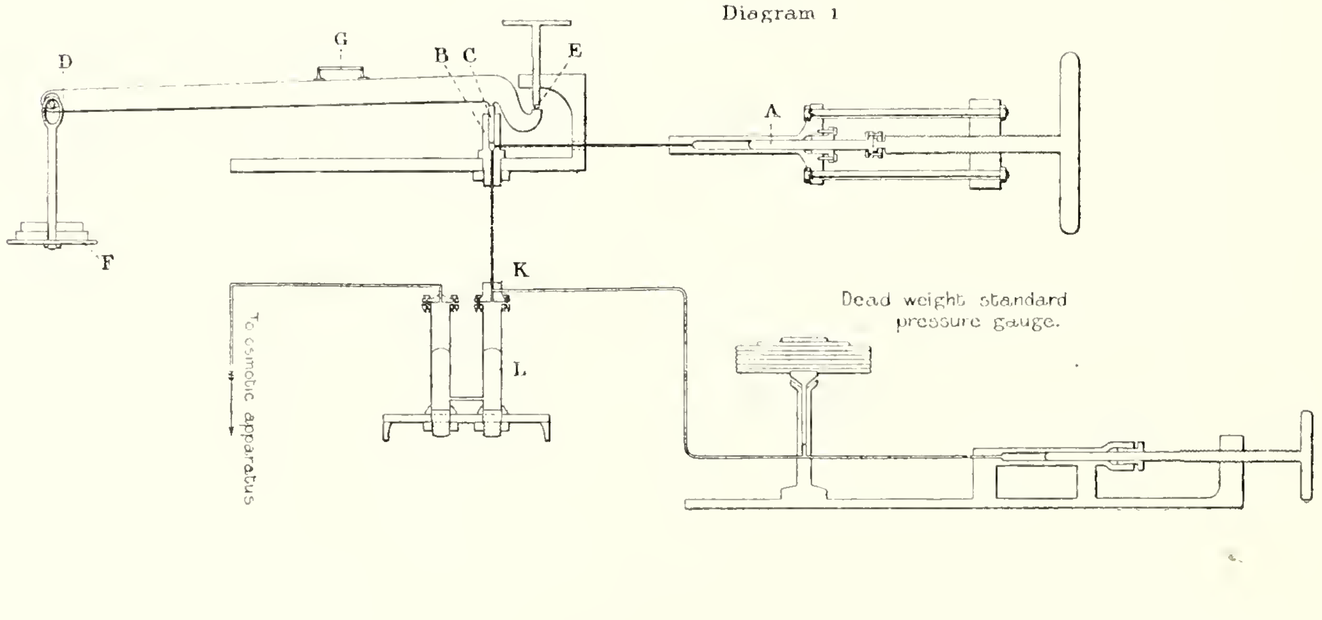


Diagram 1



A plunger A, working through a stuffing box in a cylinder, compresses a thick "steam cylinder" oil. The pressure is communicated to another cylinder B by steel pressure tubing, and a steel plunger C works vertically in B and actuates the beam DE, which has a fulcrum at E. A pan F, suspended on knife edges, carries the weights, and a sensitive level is provided at G. The beam, on account of small leakages, does not remain horizontal, but has to be relevelled at intervals by means of the plunger A.

A horizontal arm HI (see plan) is secured to the top of the plunger C (elevation) and is constrained to move to and fro by means of an oscillating system (not shown) worked from the laboratory shafting. Although the plunger works in its cylinder without any stuffing box, and the viscosity of the oil is the only preventive of large leakage, it was found advisable to move it continuously about its vertical axis—otherwise the pressure registered by the weights on the beam was not quite the same as the pressure delivered to the osmotic apparatus.

Knowing the weights on the pan, the ratio of the arms of the beam and the diameter of the plunger, the pressure can be calculated—it was noticed, however, that, when big pressures were used, the calculated values did not quite agree with those shown by a standard pressure gauge—doubtless this was caused by a slight flexure in the beam.

The cylinder B is in communication with a **U** tube L, and the pressure is delivered on to the surface of the mercury—the mercury in the other limb of the **U** tube passes on the pressure to the solution in the osmotic apparatus.

The Dead-Weight Standard Pressure Gauge.

During the course of the experiments it was found that more concordant results could be obtained than had been anticipated. The beam apparatus already described only gave pressures agreeing among themselves to about 1 per cent.; this was surmised to be due to the fact that the hardened steel balls at the fulcrum and at the top of the plunger gradually crushed the metal under them so as to form a depression, thus slightly altering the effective ratio of the arms of the beam every time it was put up. That some such effect was produced is shown by the fact that the oscillation of the arm HI (Diagram 2) caused a vertical oscillation in the beam, especially when the movable metal piece at the top of the plunger (not shown in the diagram) was worn into a depression.

It was therefore decided to substitute one of Messrs. SCHÄFFER and BUDENBERG's dead-weight standard plunger gauges for the final determination of the equilibrium pressures; this apparatus was connected to the **U** tube at K, and a tap (not shown) was provided in the **U** tube head so that the beam apparatus could be cut off when required.

The dead-weight gauge, which is a commercial article, need only be described briefly; it consists of two plungers, one supporting the weights, while the other, actuated by a screw and wheel, compresses the "steam cylinder" oil which lies between them. The plunger supporting the weights may be regarded as the pressure gauge of the instrument; it was kept slowly rotating by hand whenever it was in use. The apparatus can be worked up to 136 atmospheres. The sensibility throughout the whole range is about 0·12 atmosphere, consequently at low pressures the percentage error is considerable.

The apparatus was compared with a standard Bourdon gauge and found correct. It should be borne in mind that the total pressure on the solution is the pressure registered by the dead weight together with that of the atmosphere.

The Semi-Permeable Membranes.

The membranes were deposited on the surface of the porcelain tubes by the following means. The porcelain tube is placed in a copper sulphate solution (50 grammes in a litre) in a desiccator and the air exhausted, until no more bubbles come off from the tube—this takes place only after several days—the tube is withdrawn, wiped inside and outside with a clean linen duster, and allowed to dry for $\frac{3}{4}$ hour. The ends are then closed by rubber plugs, perforated for the passage of glass rods; then, holding the tube horizontal and spinning it rapidly between the fingers, it is plunged into a solution of potassium ferrocyanide (42 grammes in a litre). By this means an even deposit of copper ferrocyanide, very close to the outer surface of the porcelain, is obtained. The tube is allowed to soak in the ferrocyanide, after which it is set up for electrolysis. The same solutions and of the same strength are used; the tube is plugged at one end, and at the other is fitted with a perforated plug and thistle funnel, through which a copper electrode dips into the copper sulphate solution, while a platinum electrode is immersed in the ferrocyanide surrounding the porcelain tube. It was found best to place the platinum electrode in a porous pot suspended in the ferrocyanide solution, in order to prevent the alkali from attacking the membrane, and the solution in the pot was frequently changed during the experiment.

The current is passed (from the copper to the platinum electrode) until the resistance becomes constant; this generally takes about 2 hours. We found, as noted by Messrs. MORSE and HORN[*], that apparently the best voltage to apply is a hundred volts. When the resistance has risen to a steady value, the tube is taken out, washed and allowed to soak in distilled water for about ten days; care should be taken that the last traces of copper sulphate are not washed away. Experiment showed that unless this substance be present, the colloid copper ferrocyanide begins to dissolve. It may be mentioned that, before the necessity of this precaution was realised, we spoilt nearly the whole of our membranes; only one of them regained its efficiency and that only after several months' work on it.

[*] 'American Chem. Jour.,' vol. 26.

After this washing, any copper ferrocyanide which is only loosely adhering to the tubes, and not deposited in the pores, is rubbed off with pumice stone, and the tube is remade electrolytically. In general the resistance increases; when steady, the tube is again washed, and the operation repeated after the lapse of a few days, and so on until there appears to be no further rise in the resistance. If the tube is a good one, the resistance should now be of the order of 50,000 ohms.

It is then set up in the osmotic apparatus and tested with a solution of 660 grammes of cane sugar in the litre—a solution whose equilibrium pressure is about 100 atmospheres; the tube will probably give a turning point somewhat lower than this pressure, on account of a leak of solution through the membrane. The tube is then taken down, electrolytically remade, soaked in water for two or three days, and tested again with the cane sugar. It will be found that although there has been no apparent rise in the resistance, the turning-point pressure has perceptibly increased. The whole process is again repeated until a final steady value of the turning point is reached. A determination of the amount of sugar that has come through the membrane during an experiment will help to indicate whether the tube is likely to be of any use or not.

The following table shows the progress of a certain tube which will be called N; the membrane was originally deposited on it about March 8, 1904.

TABLE I.

Date.	Resistance.	Temperature.	Turning point.	Temperature.
	ohms		atmospheres	
March 11, 1904	2,700	Laboratory	—	Laboratory
November 4, 1904	29,000	„	—	„
„ 15, 1904	38,000	„	—	„
December 12, 1904	70,000	„	—	„
August 11, 1905	45,000	„	—	„
September 21, 1905	60,000	„	—	„
December 6, 1905	65,000	„	95·5	„
„ 10, 1905	300,000	0° C.	96·3	0° C.
„ 13, 1905	250,000	0	96·7	0
„ 30, 1905	250,000	0	99·4	0
January 11, 1906	200,000	0	100·0	0
„ 22, 1906	270,000	0	100·0	0
February 9, 1906	200,000	0	100·4	0
„ 25, 1906	170,000	0	These numbers refer to the resistance of the tube when "remade" after experiments with other solutions.	
March 6, 1906	170,000	0		
„ 10, 1906	170,000	0		
„ 14, 1906	170,000	0		
„ 24, 1906	170,000	0		
April 2, 1906	170,000	0		
„ 17, 1906	100,000	0		
„ 25, 1906	100,000	0		

The second column gives the resistances which the tube reached when remade—the order of number only is given; they were measured by means of an ordinary Weston ammeter. It should be mentioned that we are not quite sure that the first four entries really belonged to tube N—the record was unfortunately mixed up with that of other tubes; the numbers give, however, the usual course of events. The third column states the temperature at which the tube was remade.

The fourth column gives the turning point, obtained shortly after "remaking," when using a solution of 660 grammes of cane sugar in the litre, and the fifth column gives the temperature at which this was determined.

Out of some 100 tubes of various makes only two reached the state of efficiency shown by N, although over 400 electrolyses were made. Some of the tubes could be discarded immediately after first depositing the membrane upon them; others could never be made to reach a resistance of even 50,000 ohms, while a small percentage always allowed a fairly large amount of sugar solution to pass through them when tested in the osmotic apparatus, although their resistances appeared to be high enough.

In the course of the experiments it was found that better results were obtained if the membranes were electrolytically remade after every osmotic pressure determination, and also that, for observations at 0° C., to which this communication is restricted, it was best to remake the membrane at 0° C., and to keep the tubes in water surrounded by ice during the time elapsing between "remaking" and setting up for an experiment.

Remaking the Membranes under Pressure.

All the tubes (except N) which, judging by their resistances, seemed promising, were also remade electrolytically under pressure. The object aimed at was to break down the weak places in the membrane while the current was passing, so that any small holes would be filled up at once by the interaction of the copper and ferrocyanide ions. It is probable that the pressure alone causes a considerable part of the improvement by forcing the membrane into the pores of the porcelain. It will have been noticed that in the previous table the resistance of N on December 10, 1905, suddenly rose from 65,000 ohms to 300,000 ohms; this may be due to either of the two changes in the conditions, *i.e.*, to having previously been subjected to pressure, or to the change in the temperature at which the membrane was remade; we have found that both causes improve the membranes.

The apparatus for remaking the membranes under pressure is shown in Diagram 3. AB is a strong wrought-iron cylinder* which can be connected to the U tube mentioned on page 485 by means of the steel pressure tubing C. The apparatus is filled with a strong solution of cane sugar,† in which the usual quantity of potassium ferrocyanide has been dissolved; the equilibrium pressure of the solution should be about 130 atmospheres. The porcelain tube, M, filled with the copper sulphate solution, is suspended in the sugar solution by means of the arrangement shown at D; this consists in a glass capillary EF, furnished with a thistle funnel at H, and down which a platinum wire is threaded. The lower end of the platinum is connected to a copper coil. A tight joint between the glass capillary and the porcelain tube is made by blowing a conical bulb in the former and inserting the taper end into the rubber plug I. The bottom of the tube is closed in a similar manner.

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* It is capped by a lead washer, as indicated in the diagram.

† The object of the sugar solution was (1) to preserve such parts of the membrane as were already good by preventing a great flow of water through them, (2) to prevent, by its great viscosity, the alkali, which is found at the walls of the cylinder, from reaching the membrane.

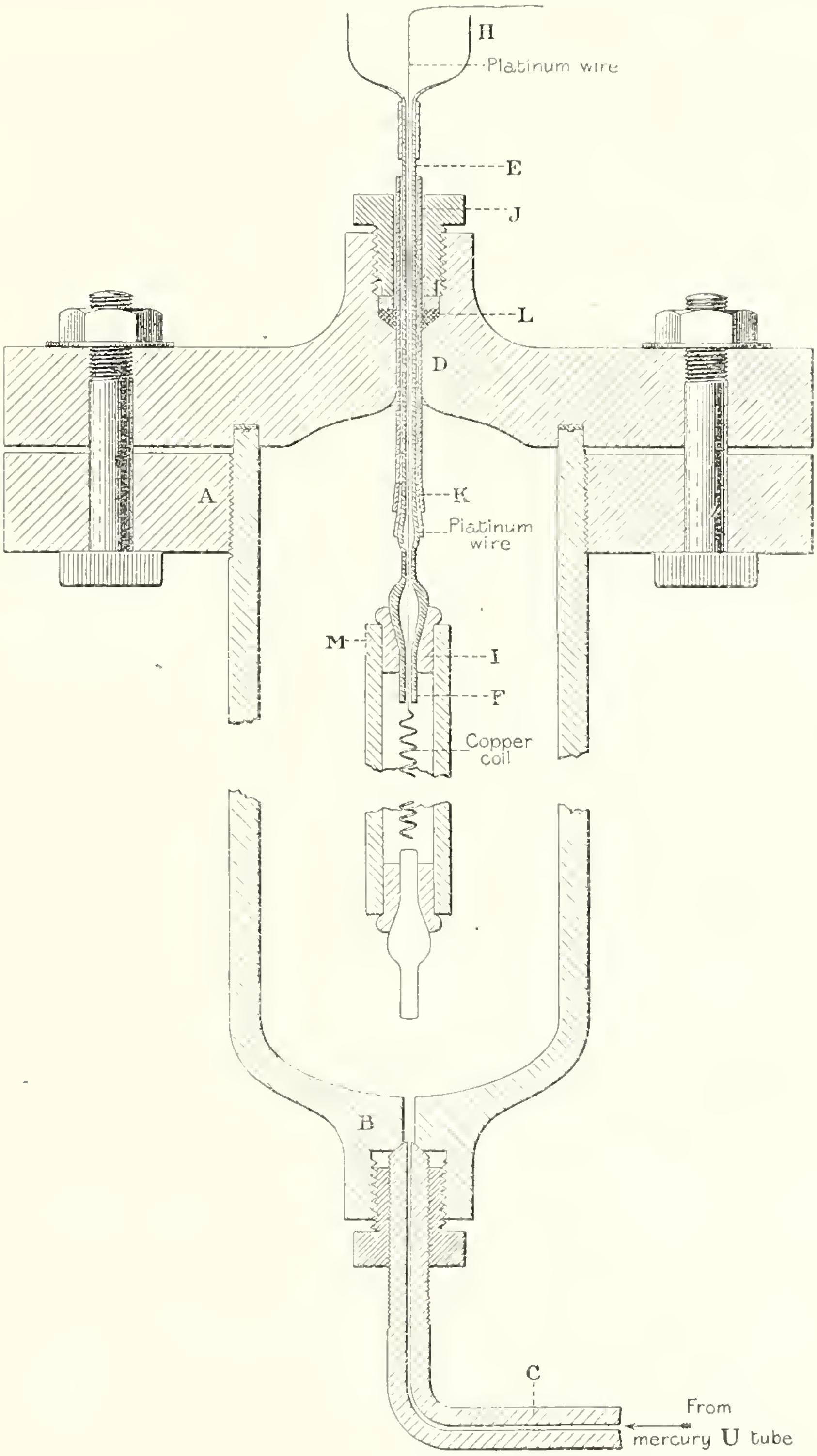

Diagram 3.

A brass tube JK surrounds the capillary, and the joint between the two, at K, is made by slipping a piece of rubber tubing over a slight thickening in the capillary.

The brass tube serves to protect the glass from the pressure exerted by the dermatine ring L, when it is compressed by the nut and washer.

It will be observed that by this arrangement the outside surface of the porcelain can be subjected to pressure while the inside is only under atmospheric pressure, and if the wrought-iron vessel be connected to one terminal of the battery and the platinum wire to the other, a current can be passed through the porcelain and the solutions.

Pressures of about 130 atmospheres were used.

The Operation of Determining the Equilibrium Pressure.

There are three separate operations required for the purpose of determining the equilibrium pressure.

(1) *Guard-ring Leak.*—As explained in our preliminary paper, the semi-permeable membrane is never quite on the surface of the tube, and, therefore, it is impossible to get perfect contact between the dermatine rings (see fig. 1) and the membrane. The result of this is that a small quantity of solution is forced out at this point. In the old apparatus there was always a noticeable part of the membrane not subjected to pressure, over which this solution flowed and, therefore, abstracted water from the interior. In the new apparatus, by arranging that the dermatine rings overlap the ends of the tube, we have reduced the exposed membrane to a minimum; there are, however, minute cracks in the glaze at the ends of the tubes, and the solution, flowing over these, draws water from the interior. To ensure that the rate at which the water is abstracted is constant during an experiment, the metal tubes VV (see fig. 1) were provided and were filled with enough solution to cover the ends of the porcelain.

The amount abstracted, that is, the guard-ring leak, was determined before every observation in the following manner. The tube was set up in the osmotic apparatus and the latter was filled with water, filling the porcelain tube as well; the pressure tube T (see fig. 1) was replaced by an open glass tube, which was filled with water to the same level as that of the water in the capillary gauge; the whole apparatus was then placed in ice, and some of the solution whose equilibrium pressure was afterwards to be determined was poured into VV.

When the temperature, indicated by a thermometer placed in mercury in a hole bored some distance into the osmotic apparatus, had fallen nearly to 0° C., and was constant at that point, repeated measurements of the rate at which the water in the gauge fell were made until constant rates were obtained; the latter were taken to be due to the guard-ring leak.

The guard-ring leak, which in our previous work had been equivalent to a rate such as would be produced by a pressure of two or three atmospheres on the solution, was now found to be very nearly negligible and corresponded to about 0·15 of an atmosphere; it was also nearly constant for any one tube, as will be seen on reference to the table of results.

(2) *Determination of the Turning Point.*—As already explained, a gradually increasing pressure is put upon the solution until the level of the water in the gauge ceases to fall and begins to rise. If there were no corrections to apply, the pressure at which this turning point takes place would give the equilibrium pressure; but on account of the guard-ring leak, and the solution leak (see later), the turning point is not, in general, the pressure required.

The method therefore adopted is to take rates of movement of the level in the gauge, corresponding to slightly differing pressures, both below and above the turning point; any small correction can then easily be applied.

The operation, then, is first to determine the guard-ring leak; after this the apparatus is withdrawn from the ice and the water outside the porcelain tube run out, and, after washing with a portion of the solution, it is filled with that solution—with very viscous solutions it is advisable to use a force pump. The washing and the filling should be carried out as rapidly as possible, for it must be remembered that until the equilibrium pressure can be put on the solution, the latter is in contact with the membrane and is diluting itself by abstracting water from the inside of the tube. When full, the apparatus is replaced in ice and connected to the beam pressure apparatus. Weights are then put on the pan, and at the same time the beam is kept horizontal by means of the wheel and screw and its plunger. The weights are put on the pan by increments of 2 and 3 kilos—this represents 8 or 12 atmospheres—at short intervals of time; a very rapid addition of weights might strain the membrane, while the sudden application of the equilibrium pressure would almost certainly damage it. When within about 10 per cent. of the equilibrium pressure, the weight increment is reduced and the length of time between the changes is increased; for it is found that the water, which had been sucked into the solution during the filling, will, on account of imperfect diffusion, now be squeezed out again, and it was feared that a rapid flow of water through the membrane might be detrimental. The weights are added in this manner until the turning point is about reached; then an interval of an hour is allowed to elapse to give time for the temperature throughout the apparatus to become steady at 0° C., and also for the more dilute stratum of solution near the membrane to diffuse.

In the later experiments we proceeded as follows:—The dead-weight gauge, previously adjusted to give a pressure close to that already on the solution, is turned on and the beam apparatus cut off. The weights are then rapidly adjusted until the rate of movement in the water gauge is as nearly as possible equal to the guard-ring leak. If the exact pressure cannot be applied by the weights we use (the increment of weight is equivalent to 0·34 atmosphere), a rate slightly above or slightly below the turning point is taken. The dead-weight gauge is then cut off and the beam apparatus turned on.

At intervals of an hour the same process is repeated until we are satisfied that no further change in the rate corresponding to a given pressure will take place. Two rates, one above and one below the turning point, are then considered to be sufficient to enable that point to be calculated.

With viscous solutions, such as 660 grammes of cane sugar, it was necessary to lengthen the interval of time considerably; in fact, a constant rate was generally only attained after the apparatus had been set up for some 5 or 6 hours.

In the earlier experiments, before we realised that the method was susceptible of greater accuracy, we used somewhat larger increments of pressure. It was found that there were slight differences in the rate corresponding to a given pressure according as that pressure had been reached from above or below. A moment's consideration will show the cause of this.

It is evident that for any definite pressure, unless it be exactly the turning-point pressure, the solution near the membrane must be changing in concentration; the change is brought about by the water which is either squeezed out or sucked into the solution. This layer of abnormal concentration is prevented from merging rapidly into the remainder of the solution, because it is entangled in the pores of the porcelain tube lying outside the membrane, so that on taking off weights, when working above the turning point, the observed rate is that due to a slightly more concentrated solution than normal, while when working below it is due to a more dilute one.

The following table gives an example of the kind of effect produced. It is extracted from the laboratory notebook, and gives part of the experiment of August 23, with 420 grammes of cane sugar.

TABLE II.

	Temperature of osmotic apparatus.	Pressure on the solution in atmospheres.	Gauge readings.	Rate of movement in millimetres per 15 minutes.*
	° C.			
5.10 P.M.	0·13	41·80	—	—
5.12 ,,	—	41·80	276·6	−12·2
5.20 ,,	—	42·77	270·1	
5.22 ,,	—	42·77	271·4	− 5·1
5.30 ,,	—	43·74	268·7	
5.32 ,,	—	43·74	270·8	+ 0·9
5.40 ,,	—	44·71	271·3	
5.42 ,,	—	44·71	274·4	+ 7·1
5.50 ,,	0·15	45·68	278·2	
5.52 ,,	—	45·68	282·2	+13·9
6.0 ,,	—	44·71	289·6	
6.2 ,,	—	44·71	288·1	+ 6·4
6.10 ,,	—	43·74	291·5	
6.12 ,	—	43·74	289·8	+ 0·2
6.20 ,,	—	42·77	289·9	
6.22 ,,	—	42·77	287·3	− 5·6
6.30 ,,	—	41·80	284·3	
6.32 ,,	—	41·80	281·0	−11·6
6.40 ,,	0·18	42·77	274·9	
6.42 ,,	—	42·77	276·2	− 4·3
6.50 ,,	—	42·77	273·9	

* The rate of movement is placed opposite the pressure causing it.

We give this example in detail, as we thought at first that the error introduced from this cause might be considerable; but even in this case it is evident that it is quite small, and in our later experiments, where care has been taken not to work far from the turning point and the increment of pressure is smaller, the error is quite negligible.

(3) *Solution Leak.*—The turning point having been satisfactorily determined, the osmotic apparatus is taken apart, and the porcelain tube, with the brass tubes LL (see fig. 1) untouched, and therefore still containing the water used in the experiment, is placed in distilled water. After an interval of two or three days, about 100 cub. centims. of water are run through the tube and the content of sugar analysed. If enough sugar is found, another 100 cub. centims. are run through at the end of two more days, and this process is repeated until there is practically no more sugar in the tube. It is then remade electrolytically at 0° C., and kept in water at that temperature.

We would like to point out that even with the best membranes there is always, or nearly always, an indication of a very small quantity of sugar as having come through the membrane,[*] and we would therefore emphasize the necessity of always testing the water inside the tube.

The analyses were made by means of FEHLING'S solution; the equivalent value, in terms of sugar, of the resulting copper oxide, together with a standard method of working, being obtained by the analysis of dilute solutions of sugar of known content.

In our preliminary paper we stated that, on certain assumptions, a satisfactory correction for the solution leak could be applied to the apparent turning point so as to give concordant results; at that time the membranes were new, and a fairly large amount of sugar came through during the whole time an experiment lasted. We now find that with the very much improved membranes—membranes it must be remembered which undoubtedly have given way some scores of times, and been remade in probably a different layer of the porcelain—there is only a rough connection between the amount of solution leak and the lowering of the turning point. It is evident that, apart from the difficulties of analysis, with such small quantities of sugar no exact connection could be expected; the extremely minute holes in the membrane, indicated by the smallness of the leak, may easily close up or open out during the course of the experiment. All attempts, therefore, to correct for the "solution leak" were given up, and the value of an experiment was based on the amount of sugar found inside the tube; practically this resolved itself into rejecting, for the final computation of the equilibrium pressure, all the experiments done with tubes other than those we call X and N, and only accepting these when it had been proved that no more sugar than 0·0003 gramme had come through in the experiment.

The following table, copied from the laboratory notebook, gives examples of the

[*] *Cf.* Table VI., Column VII.

experiments—they cover the whole range of pressures. The first of the two columns headed pressure gives the approximate pressure in atmospheres corresponding to the weights on the beam; the second gives the accurate pressure delivered by the dead-weight standard gauge. The next column gives the height of the level of the water in the glass capillary at the times shown. The seventh column gives the rate of movement of the water level for 15 minutes, and the numbers are placed opposite to the pressures causing the movement.

The process pursued will be clear from the following example. Referring to the experiment with dextrose, begun May 17, at 12.5 P.M., the height of the water was 236·3 millims.; immediately this level had been noted, the pressure was altered to 28·92 atmospheres, and a short interval of time allowed for a steady state to be reached; at 12.10 the level was at 234·9 millims. Ten minutes after, at 12.20, the level had fallen to 233·2. The difference between the last two readings gives the rate corresponding to 28·92 atmospheres pressure.

TABLE III.—Experiment with 200 grammes of Dextrose in the litre with Tube X. (R = 111,000 ohms.)

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Date.	Time.	Temperature of osmotic apparatus.	Pressure.		Reading of water level in gauge.	Rate of movement of water in millims. per 15 minutes.	Rate corrected for G.R.L.	Remarks.
			Pressure given by beam in atmospheres.	Dead-weight pressure in atmospheres.				
		° C.						
March 17 .	5.0 P.M.	—	—	—	—	—	—	Set up for G.R.L. in ice.
„ 18 .	5.15 „	0·05	—	—	258·2	—	—	
	6.20 „	—	—	—	255·5	0·6	—	
	7.5 „	—	—	—	253·7	0·6	—	
„ 19	9.35 A.M.	—	—	—	—	—	—	Set up for O.P. in ice.
	9.38 „	—	29·4	—	—	—	—	
	10.47 „	0·04	—	28·92	—	—	—	Cut off beam apparatus.
	10.50 „	—	—	28·92	230·9	−3·0	—	
	10.55 „	—	—	29·26	229·9	—	—	
	11.0 „	—	—	29·26	230·7	+0·3	—	
	11.5 „	—	29·4	—	230·8	—	—	Cut off dead weight.
	11.50 „	0·04	—	29·26	—	—	—	Cut off beam apparatus.
	11.55 „	—	—	29·26	235·9	+0·6	+1·2	
	12.5 P.M.	—	—	28·92	236·3	—	—	
	12.10 „	—	—	28·92	234·9	−2·5	−1·9	
	12.20 „	—	—	28·92	233·2	—	—	Took down and set up for "solution leak."
„ 21 .	9.0 A.M., 100 cub. centims. run through the tube gave 0·0007 gramme of sugar.							

The rate for a pressure of 29·26 atmospheres is +0·6 millim. in 15 minutes.
„ „ „ 28·92 „ −2·5 millims. „

Therefore a difference of pressure of 0·34 atmosphere causes a difference in the rate of 3·1 millims., hence the correction to be subtracted from 29·26 atmospheres to obtain the pressure at which no movement of the water would have taken place, that is, the apparent turning point, is 0·6 × 0·34/3·1 = 0·06 atmosphere. The apparent turning point is, therefore, 29·20 atmospheres. As the "guard-ring leak" is also 0·6 millim. in 15 minutes, the correction to be subtracted from the apparent turning point will also be 0·06 atmosphere, and the corrected turning point is 29·14 atmospheres.

TABLE IV.—Experiment with 540 grammes of Cane Sugar in the litre with Tube X. (R = 143,000 ohms.)

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
			Pressure.					
Date.	Time.	Temperature of osmotic apparatus.	Pressure given by beam in atmospheres.	Dead-weight pressure in atmospheres.	Reading of water level in gauge.	Rate of movement of water in millims. per 15 minutes.	Rate corrected for G.R.L.	Remarks.
		° C.						
Oct. 22	10.0 A.M.	—	—	—	—	—	—	Set up for G.R.L. in ice.
	5.0 P.M.	—	—	—	310·5	—	—	
	5.10 ,,	—	—	—	309·8	1·0	—	
,, 23	8.20 A.M.	—	—	—	256·8	—	—	
	8.30 ,,	—	—	—	256·3	0·8	—	
	9.28 ,,	—	—	—	—	—	—	Set up for O.P. in ice.
	10.55 ,,	0·15	67·1	—	—	—	—	
	12.5 P.M.	0·06	—	67·37	—	—	—	Cut off beam apparatus.
	12.7 ,,	—	—	67·37	358·7	−1·7	—	
	12.15 ,,	—	—	68·05	357·8	—	—	
	12.17 ,,	—	—	68·05	359·4	+3·4	—	
	12.25 ,,	—	—	67·37	361·2	—	—	
	12.27 ,,	—	—	67·37	359·8	−2·1	—	
	12.35 ,,	0·06	67·5	—	358·7	—	—	Cut off dead weight.
	3.5 ,,	0·04	—	67·37	—	—	—	Cut off beam apparatus.
	3.10 ,,	—	—	67·37	364·9	−2·0	−1·2	
	3.20 ,,	—	—	68·05	363·6	—	—	
	3.22 ,,	—	—	68·05	365·0	+3·4	+4·2	
	3.30 ,,	—	—	67·37	366·8	—	—	
	3.32 ,,	—	—	67·37	365·1	−2·1	−1·3	
	3.40 ,,	—	—	68·05	364·0	—	—	
	3.42 ,,	—	—	68·05	365·6	+3·2	+4·0	
	3.50 ,,	—	—	67·37	367·3	—	—	
	3.52 ,,	—	—	67·37	365·8	−2·1	−1·3	
	4.0 ,,	—	—	67·37	364·7	—	—	Took down and set up for "solution leak."
,, 26 . .	7.30 A.M., 100 cub. centims. run through the tube gave no trace of sugar.							

In a manner similar to that detailed in the previous experiment, the apparent turning point is 68·08 − 3·2 × 0·68/5·3 = 67·67 atmospheres, and the corrected turning point is 67·67 − 0·8 × 0·68/5·3 = 67·56 atmospheres.

TABLE V.—Experiment with 750 grammes of Cane Sugar in the litre with Tube X. (R = 111,000 ohms.)

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
			Pressure.					
Date.	Time.	Temperature of osmotic apparatus.	Pressure given by beam in atmospheres.	Dead-weight pressure in atmospheres.	Reading of water level in gauge.	Rate of movement of water in millims. per 15 minutes.	Rate corrected for G.R.L.	Remarks.
		° C.						
March 27 .	5.0 P.M.	—	—	—	—	—	—	Set up for G.R.L. in ice.
,, 28	9.6 A.M.	—	—	—	242·9	—	—	
	9.26 ,,	0·05	—	—	242·2	−0·5	—	
	9.55 ,,	—	—	—	—	—	—	Set up for O.P. in ice.
	10.5 ,,	—	132·0	—	—	—	—	
	10.50 ,,	—	134·0	—	—	—	—	
	11.45 ,,	0·04	—	132·69	—	—	—	Cut off beam apparatus.
	11.50 ,,	—	—	132·69	258·0	−1·5	−1·0	
	11.55 ,,	—	134·0	—	257·5	—	—	Cut off dead weight.
	12.35 P.M.	—	—	133·37	—	—	—	Cut off beam apparatus.
	12.40 ,,	—	—	133·37	274·4	+1·5	+2·2	
	12.45 ,,	—	134·0	—	274·7	—	—	Cut off dead weight.
	2.40 ,,	—	—	133·37	—	—	—	Cut off beam apparatus.
	2.45 ,,	—	—	133·37	308·7	+0·1	+0·6	
	2.55 ,,	—	134·0	—	308·8	—	—	Cut off dead weight.
	5.0 ,,	—	—	133·37	—	—	—	Cut off beam apparatus.
	5.5 ,,	—	—	133·37	342·2	−0·1	+0·5	
	5.15 ,,	—	—	133·03	342·1	—	—	
	5.20 ,,	—	—	133·03	341·0	−1·3	−0·8	
	5.30 ,,	—	—	—	340·1	—	—	Took down and set up for "solution leak."
,, 30 .	9.0 A.M., 100 cub. centims. run through the tube gave 0·0009 gramme of sugar.							
April 1 . .	9.0 ,, 100 ,, ,, ,, ,, 0·0013 ,, ,,							

NOTE.—The "solution leak" was not pursued any further on account of our absence from the laboratory.

The apparent turning-point pressure is 133·42 atmospheres.

The corrected turning point is 133·23 atmospheres.

This experiment was selected so as to give an idea of the influence that a small solution leak has on the experiments. It will be noticed on examining the tabular statement of results that the experiment gives a value of the turning-point pressure slightly below another experiment where there was practically no leak.

Substances Used.

For the cane-sugar solutions, "double refined" loaf sugar was used; it was tested for invert sugar and only a trace found; tests were also made of the solution at the end of an experiment, and the quantity of invert sugar showed a scarcely appreciable increase.

The solutions, both for cane sugar and for the other substances, were always made up the night before an experiment.

The dextrose was purchased from Messrs. KAHLBAUM, and was described by them as their purest anhydrous; no tests as to purity were made except to determine the amount of moisture* in the various quantities sent. The amount was found to be very small and practically constant. The galactose was also KAHLBAUM'S purest anhydrous; the amount of moisture was found to be constant. Some of the galactose was recovered by crystallizing from a saturated solution and digesting with methyl alcohol for 10 days. Solutions of 500 grammes of this recovered galactose in the litre gave equilibrium pressures (see table of results) which were about 2 per cent. higher than those obtained with similar solutions of the original substance. As the purification of galactose is a very lengthy process, and our main object in making experiments with this substance was to see if it be suitable for osmotic pressure measurements, no further steps have yet been taken in the matter. The mannite came from KAHLBAUM, and was only tested for moisture.

A considerable number of organic substances which are not likely to be dissociated in aqueous solutions were tried, but without success, as they all passed through the membranes to a greater or less degree.

Results.

In the following tables we give all the experiments that we have made at 0° C., with the exception of those which were carried out merely for the purpose of testing the membranes. The concentration of the solution is placed at the head of each table; the numbers are the weights of the substance in one litre of solution made up at 15° C.:—

Column (I.) gives the date of the experiments; these are tabulated in chronological order.

Column (II.) gives the name of the tube used.

Column (III.) gives the apparent turning-point pressure, in atmospheres, as derived from the dead-weight standard pressure gauge. It is the pressure for which there would have been no movement of the water in the capillary gauge.

A blank in the column means that the true turning-point pressure was exactly that on the solution, and therefore it was not necessary to take rates above and below it; in other words, this pressure gave a rate which exactly equalled the "guard-ring leak" rate.

Column (IV.). In this and the other columns where rates are given it is to be noted that they all represent the movement of the level of the water in the capillary in millimetres per 15 minutes. The rates in this column are those caused by the "guard-ring leak."

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* The "moisture" was determined by the loss of weight of the substance on heating at 100° C.; but we have evidence that there were traces of methyl alcohol present.

Column (V.) gives the apparent turning-point pressure corrected for the "guard-ring leak" (see explanation of column X.). As already pointed out, the pressures registered by the dead weights are not the total pressures on the solution; the pressure of the atmosphere must be added to them. On the other hand, the water inside the tube is under atmospheric pressure, so that if there had been no "solution leak" the pressures noted in this column would be equilibrium pressures.

Column (VI.) gives the length of time the solution was under pressure.

Column (VII.) gives the total amount, in grammes, of solid which came through the membrane during the experiment. The letters j.v.t. mean "just visible trace."

Column (VIII.). Assuming that the amount of solid given in (VI.) represents a corresponding volume of solution, then the numbers in this column give the rate at which the water would rise in the gauge, on the further assumption that the solution came through the membrane at a uniform rate.

Column (IX.) gives the increment of pressure, in atmospheres, which was used in the experiment. Column (X.) gives the difference between the rates corresponding to the two pressures separated by this increment, the one just above and the other just below the turning point. The numbers are therefore the rates due to these increments of pressure near the turning point. It is from these rates that the correction for the "guard-ring leak" is derived by assuming that it bears the same ratio to the increment of pressure as the numbers in (IV.) do to those in (X.).

TABLE VI.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Date.	Name of tube.	Apparent turning-point pressure in atmospheres.	Rate of movement of water-level due to guard-ring leak.	Turning-point pressure in atmospheres.	Time.	Solution leak.	Rate of movement of water-level due to solution leak.	The increment of pressure used in the experiment.	Rate of movement of water-level caused by increment of pressure.
					h. m.			atmospheres	
180 GRAMMES CANE SUGAR.									
Nov. 15	X	14·03	0·5	*13·96	3 35	trace	—	0·34	2·5
,, 24	X	—	0·8	*13·95	4 40	j.v.t.	—	0·34	—
300 GRAMMES CANE SUGAR.									
Oct. 4	B	26·35	0·9	26·28	5 45	0·0023	1·1†	0·68	8·3
,, 6	G	26·16	0·8	26·07	6 15	0·0016	0·7†	0·68	5·9
,, 9	X	26·78	0·8	*26·69	7 40	j.v.t.	—	0·68	6·0
,, 17	X	26·85	0·8	*26·76	5 35	none	—	0·68	5·8
Nov. 14	G	26·37	0·4	26·32	5 0	0·0014	0·7†	0·34	2·8
420 GRAMMES CANE SUGAR.									
Aug. 10	X	42·8	0·0	42·8	8 45	0·0035	0·8	0·97	5·8
,, 13	B	40·7	0·0	40·7	7 30	0·0090	4·7	0·97	6·9
,, 18	G	39·8	0·2	39·8	3 0	0·0247	15·7	0·97	6·2
,, 23	X	43·7	0·7	43·6	3 20	trace	—	0·97	7·1
,, 25	B	41·8	0·6	41·7	5 10	0·0162	5·9	0·97	7·7
,, 29	X	44·09	0·6	*44·00	6 40	trace	—	1·36	9·0
Sept. 3	G	40·3	0·2	40·2	5 10	0·0181	6·6	0·97	6·0
,, 7	X	43·49	0·5	43·40	5 30	0·0006	—	1·36	7·5
,, 12	B	43·52	0·9	43·42	5 30	0·0035	1·2†	1·36	12·0
,, 20	G	42·50	0·2	42·46	6 0	0·0083	2·6†	1·36	7·6
,, 29	X	44·14	0·7	*43·95	8 0	none	—	1·36	10·6
Nov. 23	G	43·39	0·6	43·32	5 25	0·0043	1·5†	0·34	2·9
540 GRAMMES CANE SUGAR.									
Oct. 19	G	67·26	0·3	67·22	5 55	0·0015	0·4†	0·68	4·8
,, 23	X	67·67	0·8	*67·56	6 30	none	—	0·68	5·3
,, 27	V	66·34	0·0	66·34	7 30	undetermined	—	0·34	1·8
,, 28	X	67·54	0·8	*67·43	3 0	j.v.t.	—	0·34	2·4
660 GRAMMES CANE SUGAR.									
Nov. 2	X	100·72	0·7	*100·61	7 45	j.v.t.	—	0·34	2·3
,, 3	G	100·21	0·2	100·19	8 0	0·0036	0·5†	0·34	2·4
,, 7	B	100·32	0·2	100·30	6 0	0·0171	—	0·34	3·0
,, 9	X	100·91	0·9	*100·86	5 55	none	—	0·34	3·4
Jan. 30	V	99·48	0·4	99·42	7 40	0·0077	1·2†	0·34	2·4
Feb. 14	B	100·32	0·9	100·22	6 45	0·0047	0·8†	0·34	3·2
750 GRAMMES CANE SUGAR.									
Nov. 17	V	133·45	0·1	133·44	7 10	0·0044	0·6†	0·34	2·0
March 22	N	133·88	0·5	*133·74	7 45	0·0002	—	0·34	1·2
,, 28	X	133·42	0·5	133·28	7 35	0·0022	0·3†	0·34	1·2

NOTE.—The experiments marked * are dealt with on p. 503, and those marked † in Appendix A.

Remarks.—The experiment of August 23 is rejected for the final result. It was carried out solely with the beam apparatus, and, as already stated, the degree of accuracy obtainable with that apparatus is not sufficiently good for the purpose.

The total quantity of sugar found in the experiment of November 7 is quite anomalous. We can offer no satisfactory explanation of this.

TABLE VII.

I.	II	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Date.	Name of tube.	Apparent turning-point pressure in atmospheres.	Rate of movement of water-level due to guard-ring leak.	Turning-point pressure in atmospheres.	Time.	Solution leak.	Rate of movement of water-level due to solution leak.	The increment of pressure used in the experiment.	Rate of movement of water-level caused by increment of pressure.
					h. m.			atmospheres	
100 GRAMMES DEXTROSE.									
May 16	X	13·24	0·5	*13·21	3 0	none	—	0·34	3·9
200 GRAMMES DEXTROSE.									
March 10	X	29·25	0·7	*29·18	2 15	0·0002	—	0·34	3·2
,, 19	X	29·20	0·6	29·14	2 45	0·0007	1·0	0·34	3·1
320 GRAMMES DEXTROSE.									
Feb. 26	N	50·94	0·8	50·81	3 5	0·0034	2·8	0·34	1·8
March 6	X	53·51	1·5	*53·33	2 40	0·0001	—	0·34	2·8
,, 16	N	—	0·5	52·40	2 20	0·0011	1·2	0·34	—
,, 24	X	53·09	0·5	*53·04	2 45	0·0002	—	0·34	3·2
450 GRAMMES DEXTROSE.									
Jan. 19	G	—	0·4	86·36	2 45	0·0054	3·5	0·34	—
Feb. 8	X	87·48	0·9	*87·34	3 25	0·0001	—	0·34	2·2
,, 12	X	87·84	1·1	*87·70	3 10	none	—	0·34	2·4
550 GRAMMES DEXTROSE.									
Feb. 28	X	121·09	2·8	120 66	3 10	0·0021	0·9	0·34	2·2
Mar. 8	N	121·08	0·2	*121·02	2 50	0·0002	—	0·34	1·2
May 5	X	121·46	0·9	*121·35	2 10	j.v.t.	—	0·34	2·6
,, 12	X	121·26	0·7	*121·17	2 10	0·0002	—	0·34	2·5

Remarks.—Part of the solution of May 5 was kept for a week and its equilibrium pressure redetermined on May 12. The small difference between the two results shows that no change had taken place in the interval.

TABLE VIII.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Date.	Name of tube.	Apparent turning-point pressure in atmospheres.	Rate of movement of water-level due to guard-ring leak.	Turning-point pressure in atmospheres.	Time.	Solution leak.	Rate of movement of water-level due to solution leak.	The increment of pressure used in the experiment.	Rate of movement of water-level caused by increment of pressure.
					h. m.			atmospheres	
100 GRAMMES MANNITE.									
Jan. 18	X	13·3	0·3	*13·3	2 10	0·0014	5·0	0·34	1·9
,, 26	X	—	0·5	*12·9	2 10	0·0008	2·8	0·34	—
110 GRAMMES MANNITE.									
Jan. 9	X	14·7	0·5	*14·6	2 0	0·0017	6·2	0·34	4·1
125 GRAMMES MANNITE.									
Dec. 5	X	16·71	0·5	*16·64	3 45	0·0009	1·5	0·34	2·4
,, 7	G	—	0·5	15·9	2 30	0·0066	—	0·34	—
,, 14	X	16·82	0·8	*16·71	2 0	0·0014	4·4	0·34	2·6

Remarks.—The experiments with mannite are not satisfactory; there seems to be no doubt that the membranes are slightly more permeable to this substance than to the sugars. The numbers under the heading "solution leak" are not reliable; they were obtained by evaporating down the contents of the tube and weighing the residue. Small quantities of copper sulphate left in the tube from the previous electrolytic "remaking" would help to produce higher and erratic results. No higher osmotic pressures are obtainable with mannite, as 125 grammes in the litre is about the limit of solubility.

TABLE IX.

I.	II.	III.	IV.	V.	VI.	VII.	IX.	X.
Date.	Name of tube.	Apparent turning-point pressure in atmospheres.	Rate of movement of water-level due to guard-ring leak.	Turning-point pressure in atmospheres.	Time.	Solution leak.	The increment of pressure used in the experiment.	Rate of movement of water-level caused by increment of pressure.
					h. m.		atmospheres.	
			250 GRAMMES GALACTOSE.					
Feb. 2	X	35·58	0·7	*35·47	3 35	0·0002	0·34	2·8
			380 GRAMMES GALACTOSE.					
March 14	X	62·86	0·6	*62·79	2 35	none	0·34	2·9
			500 GRAMMES GALACTOSE.					
March 12	N	—	0·3	94.59	3 10	0·0006	0·34	—
,, 26	N	—	0·3	96·63	2 12	0·0004	0·34	—
May 3	N	—	0·4	*97·31	4 15	j.v.t.	0·34	—
,, 11	N	94·92	0·7	*94·75	2 30	0·0003	0·34	1·5

Remarks.—The experiments of March 26 and May 3 were with the recovered galactose mentioned on page 497.

No higher osmotic pressures were determined, as it was found that a solution of 500 grammes in the litre was already supersaturated at 0° C.

*The Experimental Errors.**

Unfortunately we are not in a position to evaluate the experimental errors. The approximate constancy of the guard-ring leak, with different tubes, seems to justify the assumption that no great variable error enters through this cause, but it should be pointed out that we have no means of proving that there is not a constant error introduced thereby. The errors due to "solution leak" are mentioned in the next section, and are obviated by discarding those experiments which showed a leak; in this connection it should be remembered that analyses of very small quantities of sugar are far from reliable, and it may be that even the results given by those experiments which showed no trace of sugar are really too low.

It was feared that the use of a somewhat more viscous oil than the dead-weight apparatus is designed for (the makers recommend glycerine) might in cold weather vitiate the results; special experiments, however, showed this cause of error to be absent. It is scarcely necessary to point out that a sensibility of 0·12 atmosphere in the dead-weight gauge, taken in conjunction with a "guard-ring leak" rate equivalent to about 0·15 atmosphere, showed that equilibrium pressures of less than 12 atmospheres could not be measured with any degree of accuracy with this apparatus.

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* See Appendix B.

Discussion of the Results.

On looking over the tables it will be noticed that the experiments which give the highest values for the turning point are always those in which there was no "solution leak"; and the difference between these and the other results follows roughly the ratio* that the "solution leak" rate bears to the rate per increment of pressure. (In other words, the larger the "solution leak" the lower the equilibrium pressure.) No satisfactory method of correcting for these deviations was found;† so it was decided to use, for the final computation, only those experiments (marked by an asterisk) in which there was little or no "solution leak."

It has been stated already that the turning-point pressures in these experiments are the equilibrium pressures, and therefore the arithmetical mean would give the best value; but we have felt justified in giving double weight to experiments which showed no "solution leak" whatever.

The following tabular statement gives the final values for the equilibrium pressures at 0° C. of the various solutions when there is a pressure of one atmosphere on the solvent.

TABLE X.

CANE SUGAR.

180·1	grammes in the litre	gives a	pressure of	13·95	atmospheres.
300·2	,,	,,	,,	26·77	,,
420·3	,,	,,	,,	43·97	,,
540·4	,,	,,	,,	67·51	,,
660·5	,,	,,	,,	100·78	,,
750·6	,,	,,	,,	133·74	,,

DEXTROSE.

99·8	grammes in the litre	gives a	pressure of	13·21	atmospheres.
199·5	,,	,,	,,	29·17	,,
319·2	,,	,,	,,	53·19	,,
448·6	,,	,,	,,	87·87	,,
548·6	,,	,,	,,	121·18	,,

GALACTOSE.

250	grammes in the litre	gives a	pressure of	35·5	atmospheres.
380	,,	,,	,,	62·8	,,
500	,,	,,	,,	95·8	,,

RECOVERED GALACTOSE.

500	grammes in the litre	gives a	pressure of	97·3	atmospheres.

MANNITE.

100	grammes in the litre	gives a	pressure of	13·1	atmospheres.
110	,,	,,	,,	14·6	,,
125	,,	,,	,,	16.7	,,

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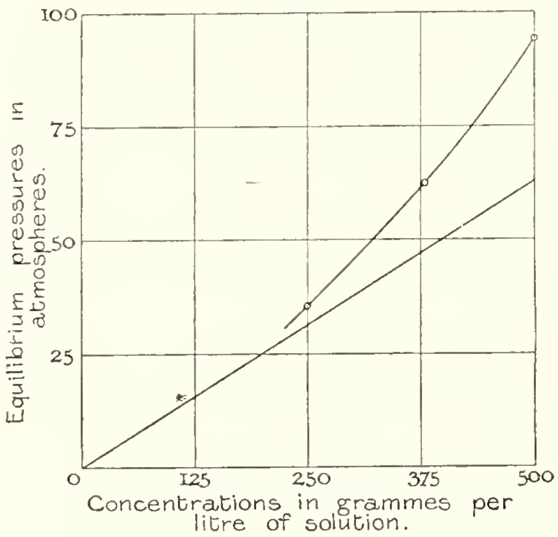
* The ratio is not tabulated, as it was not considered of sufficient importance.

† See Appendix A.

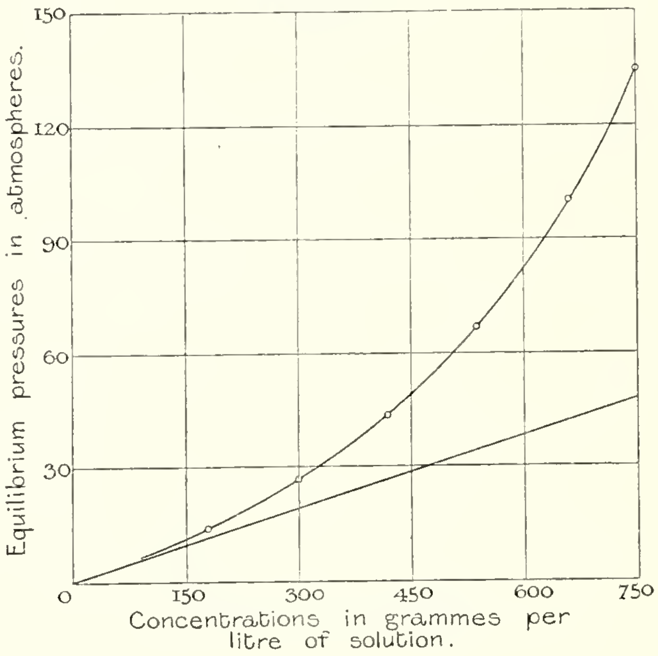
The number of grammes in the litre are, for the cane-sugar and dextrose solutions, reduced to a vacuum, the dextrose being further corrected for the small quantity of "moisture" found in the "anhydrous" substance. Neither of these corrections are applied to the galactose and mannite; in the former case because the substance is presumably slightly impure, and in the latter because the experiments are not very accurate.

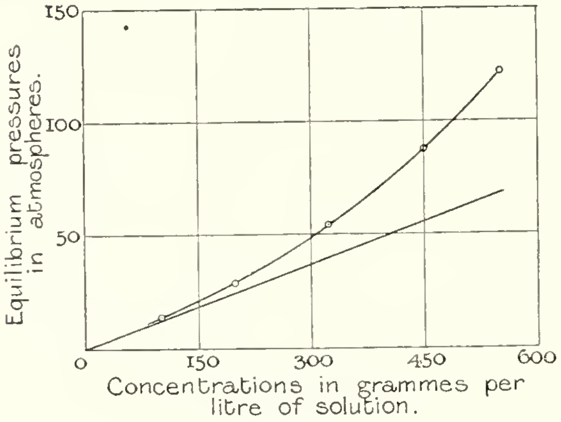
In the following set of curves the final values are plotted against concentrations, and it is interesting to observe that all four substances show considerable deviations from the straight lines which represent the theoretical osmotic pressures.* It is also to be noticed that on extrapolating the various curves towards the origin they appear to merge in the straight lines before the origin is reached; this means that dilute solutions will give pressures corresponding to the Boyle-Avogadro law, the gradients at the origin being inversely as the molecular weights of the dissolved substances.†

Galactose.

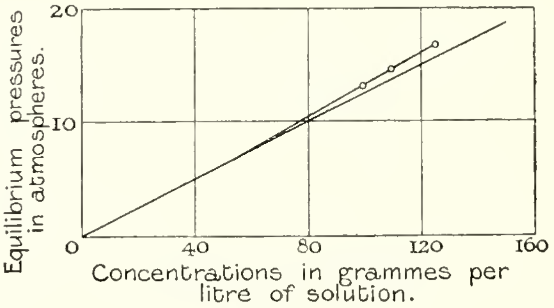


Cane sugar.





Dextrose.



Mannite.

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[*] The straight lines are drawn on the usual assumption that 1 gramme molecular weight of solute per litre should give an osmotic pressure of 22·4 atmospheres.

[†] Further consideration of the theoretical bearing of the forms of these curves is deferred.

We think that, for the purpose of comparison, it may be of use to append a table of the results (some of which have already been published) of the determination of the osmotic pressures of cane-sugar solutions by way of their vapour pressures. For the discussion of the theoretical connection and the details of the method and apparatus, we would refer to the original paper,* but would mention that a slight modification in the apparatus has enabled us to obtain more concordant values. We hope to give full details on another occasion.

TABLE XI.

Concentration in grammes per litre solution.	Temperature.	Osmotic pressure in atmospheres derived from vapour pressure.	Measured equilibrium pressure at 0° C. in atmospheres.
	° C.		
420	12·6	44·3	43·97
420	14·2	45·9	—
420	15·7	46·6	—
420	19·5	47·3	—
660	19·0	105·7	—
660	19·4	103·2	—
660	19·5	107·0	—
	LATER EXPERIMENTS.		
540	0° C.	69·4	67·51
660	0	101·9	100·78
750	0	136·0	133·74

We would draw attention to the fact that our results for cane sugar, where they overlap those obtained by Messrs. MORSE and FRASER,† are somewhat higher. For instance, a solution containing 282 grammes in the litre is given by them as having an equilibrium pressure of 22·49 atmospheres, while we obtain 25 atmospheres, this value being taken from the curve.

There seems to be no mention in Messrs. MORSE and FRASER'S account of their work of any steps taken to determine the amount of solution which came through the membranes. A small "solution leak" would make a considerable difference to the pressure they obtained, not so much on account of "back" osmotic pressure, but because the passage of a small volume of solution would have a large effect on the level of the mercury in the manometer, the more so as the diameter of the latter is only 0·5 millim. and it is a closed one. The general excellence of their work, however, makes it improbable that this hypothetical explanation is correct; it may be that future experiments will clear up the discrepancy.

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* 'Roy. Soc. Proc.,' A, vol. 77, 1906, and also 'Nature,' vol. 74, p. 6.

† 'American Chemical Journal,' vol. 34, pp. 1–99.

APPENDIX A.

[*August* 15.—An empirical method of making the correction for "solution leak" (see p. 498, explanation of Column VIII.; also p. 503) can be applied by assuming that during the passage of the solution through the minute holes in the membrane the solute has been partially filtered off from the solvent, and that this action is proportional to the concentration; if so, the rates tabulated in Column VIII. of Tables VI. and VII. must be multiplied by a factor which is proportional to the concentration.*

In the case of cane sugar, it is easy to see that this factor, for a solution of 300 grammes in the litre, is 3, and therefore for the other concentrations it will be 4·2, 5·4, 6·6, and 7·5 respectively. Then, proceeding in a manner similar to that explained at the top of p. 495, but adding the resulting pressure correction, we get, for the observations (marked †) done with the dead-weight pressure gauge, the following table, of which the results are to be compared with the numbers in Table X., where no "solution leak" is present:—

Date of experiment.	Turning-point pressure in atmospheres.	Solution-leak correction in atmospheres.	Final corrected turning-point in atmospheres.
300 GRAMMES CANE SUGAR. (Equilibrium pressure from Table X. = 26·77 atmospheres.)			
Oct. 4 . . .	26·28	0·27	26·55
,, 6 . . .	26·07	0·24	26·31
Nov. 14 . .	26·32	0·51	26·83
420 GRAMMES CANE SUGAR. (Equilibrium pressure = 43·97 atmospheres, see Table X.)			
Sept 12 . .	43·42	0·57	43·99
,, 20 . .	42·46	1·95	44·41
Nov. 23 . .	43·32	0·74	44·06
540 GRAMMES CANE SUGAR. (Equilibrium pressure = 67·51 atmospheres, see Table X.)			
Oct. 19 . .	67·22	0·31	67·53
660 GRAMMES CANE SUGAR. (Equilibrium pressure = 100·78 atmospheres, see Table X.)			
Nov. 3 . .	100·19	0·45	100·64
Jan. 30 . .	99·42	1·12	100·54
Feb. 14 . .	100·22	0·56	100·78
750 GRAMMES CANE SUGAR. (Equilibrium pressure = 133·74 atmospheres, see Table X.)			
Nov. 17 . .	133·44	0·76	134·20
March 28 . .	133·28	0·63	133·91

We propose to investigate this matter more closely. It may throw some light on the molecular structure of solutions.]

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* Almost as good an agreement is obtained if we assume that this factor is proportional to the pressure on the solution. Unfortunately the experiments with dextrose (Table VII.) are not numerous enough to differentiate between the two.

APPENDIX B.

[*August* 15.—An experiment with 750 grammes of cane sugar in the litre was made with tube N filled with a solution of 540 grammes in the litre. This experiment was carried out in a manner similar to that described in the text. The equilibrium pressure between the two solutions we found to be 66·0 atmospheres, and the difference between their equilibrium pressures as given in Table X. is 66·23 atmospheres. The agreement between these two numbers is a confirmation of the validity of the method of work.]

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